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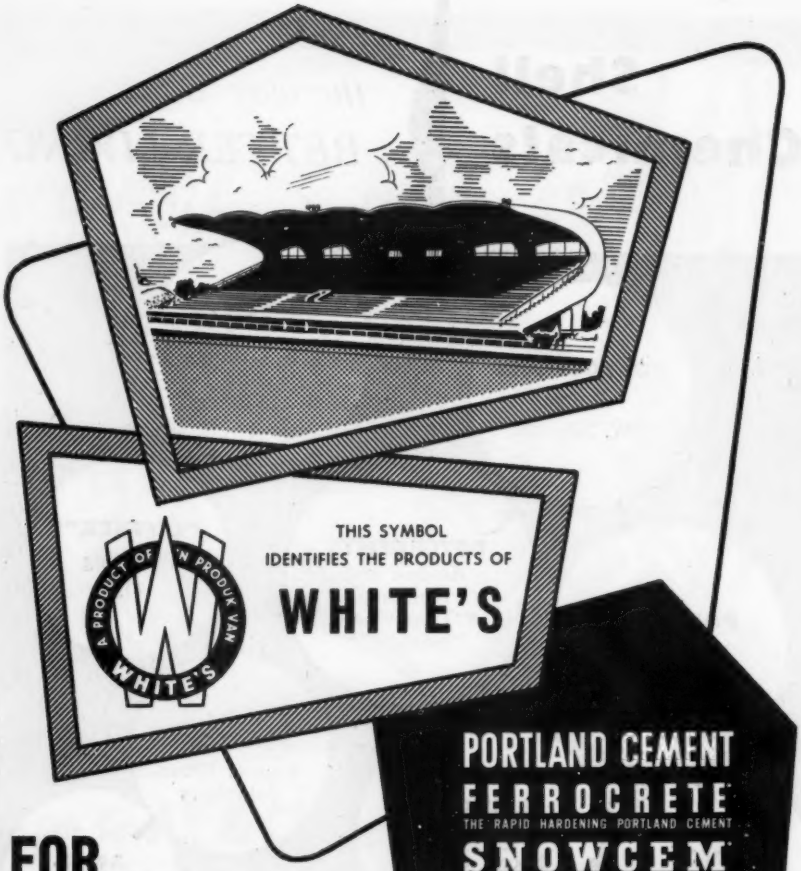

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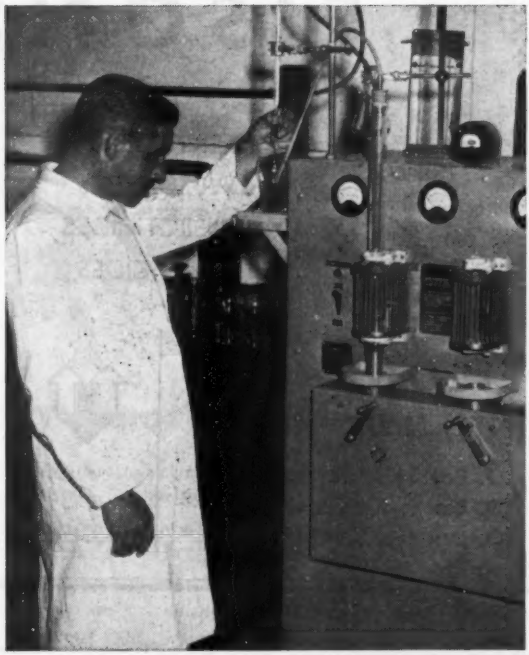

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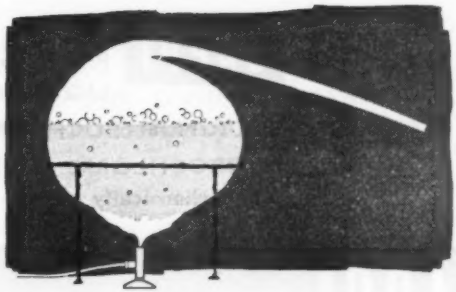

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THE SODIUM ARSENITES
PART II. ORTHO- AND PYROARSENITES*

by

J. W. MENARY

OPSOMMING

Die alkaliese natriumarseniete is gekarakteriseer deur X-straal-diffraksie waarnemings. Die chemiese struktuur van hierdie verbindings word van hulle verhouding tot natriumpolimeta-arseniet afgelei.

SUMMARY

The alkaline sodium arsenites have been characterised by X-ray diffraction measurements. The structural chemistry of these compounds is derived from their relationship to sodium polymetaarsenite.

INTRODUCTION

In part I[1] it was shown that all data in the A.S.T.M. Powder Data File (1957) for sodium arsenite are incorrect and that there is widespread confusion in the literature regarding the formulation and nomenclature of various sodium arsenites. The crystal structure of sodium polymetaarsenite was described and the polymeric nature of this compound established. The present paper characterises sodium arsenites more alkaline than sodium polymetaarsenite and indicates the structural relationships in this group of compounds.

EXPERIMENTAL

Sodium arsenites were prepared by crystallisation of solutions at about 25°C as described by Schreinemakers and de Baat[2], and by Nelson[3]. The procedure adopted by Vanzetti[4] for the preparation of trisodium orthoarsenite was followed without modification. Reagent grade chemicals were used for all preparative work. Products were analysed for Na_2O content by titration with acid, and for As_2O_3 content by iodine titration.

Powder diffraction patterns were obtained by diffractometer. Single crystal studies were made with a 6 cm diameter cylindrical camera. Nickel filtered copper radiation ($CuK\alpha_1$=1·54050Å) was used throughout.

The alkaline sodium arsenites are deliquescent, to an extent which increases with increasing alkalinity. Although powder specimens were protected by a thin film of collodion, this technique was not completely successful in preventing access of atmospheric moisture. Because some of the compounds studied dissolve incongruently, absorption of moisture can lead to the formation of different compounds. Consequently some of the powder patterns reported almost certainly include impurity lines. When it was possible to identify impurity lines by indexing the pattern, these were omitted from the data.

* A paper read in Pretoria at the Thirteenth Annual Convention of the S.A. Chemical Institute on July 22, 1959.

RESULTS

$2Na_2O.As_2O_3.xH_2O$. In that part of the phase diagram where Schreinemakers and de Baat report a single compound $2Na_2O.As_2O_3.9H_2O$, two different crystalline compounds were identified, each with a distinctive X-ray powder pattern (Tables I and II). Chemical analyses showed that the solid phases can be represented by $2Na_2O.As_2O_3.xH_2O$ where x has a value about 8 in one case and about 11 in the other.

$5Na_2O.2As_2O_3.xH_2O$. The existence at 25°C of a hydrated sodium arsenite with a molar ratio Na_2O/As_2O_3 of 2·5 was confirmed. Chemical analysis indicated that the number of water molecules, x, in the empirical formula is 25 or 26.

A crystallisation at 35°C was carried out in that part of the phase diagram where Nelson's work shows that the compound $2Na_2O.As_2O_3.7H_2O$ is the stable solid phase. The powder pattern of the solid, obtained at 25°C, was identical with that obtained for $5Na_2O.2As_2O_3.xH_2O$. Because Nelson's work indicates that the latter compound is not stable at 35°C it is probable that decomposition of the wet solid, $2Na_2O.As_2O_3.7H_2O$, had taken place as the temperature decreased to 25°C prior to the X-ray examination.

Microscopic examination showed that the crystals belong to the tetragonal system. Crystals immersed in the mother liquor dissolve with the simultaneous appearance of birefringent needles, either because of incongruent solubility effects or oxidation. The X-ray powder pattern obtained for crystals crushed and dried between filter paper changed slowly in spite of efforts to prevent access of atmospheric moisture. Table III lists the most reliable data obtained which may, however, include impurity lines.

Small single crystals of the tetragonal compound were sealed into thin-walled lithium borate capillary tubes and examined by X-ray oscillation photographs. The unit cell parameters were calculated from high angle reflections obtained using the Straumanis film mounting, giving a=6·44Å, c=22·59Å. From these figures the density calculated for a unit cell containing $5Na_2O.2As_2O_3.xH_2O$ is 2·017 g cm^{-3} for x=24 and 2·047 g cm^{-3} for x=25. The density by flotation in a density gradient was 2·012 g cm^{-3}.

$2Na_2O.As_2O_3$. In that part of the phase diagram where earlier workers report a compound of empirical formula $2Na_2O.As_2O_3$ a microcrystalline solid of the correct analysis was obtained. Because of the strongly deliquescent nature of the solid reliable powder patterns were not obtained. No crystals of sufficient size for single crystal X-ray examination could be obtained.

Na_3AsO_3. Following Vanzetti's[4] method of preparation, metallic sodium was dissolved in anhydrous methanol and reacted with the stoichiometric amount of recrystallised arsenious oxide according to the equation: $As_2O_3+6NaOCH_3=2Na_3AsO_3+3(CH_3)_2O$. The reaction mixture was heated under reflux. An attempt was made to identify any gases evolved by means of infra-red spectroscopy using a 10 cm path-length gas cell. The absorption spectrum showed the presence of methanol only, no dimethyl ether being produced. Methanol was distilled off the mixture when reaction had ceased. A highly deliquescent microcrystalline product was obtained which was extremely reactive; with chloroform a violent reaction took place liberating sodium chloride.

The powder pattern was observed to change rapidly during X-ray examination. Only those reflections which decreased in intensity during successive diffractometer

TABLE I

Powder data for disodium orthoarsenite trihydrate, $Na_2HAsO_3 . 3H_2O$

d (Å)	I
5·45	100
5·03	56
4·54	5
4·48	17
4·17	14
3·59	59
3·35	90
2·879	36
2·513	59
2·431	11

TABLE II

Powder data for disodium orthoarsenite pentahydrate, $Na_2HAsO_3.5H_2O$

d(Å)	I
10·09	20
6·53	7
5·44	37
5·03	52
4·49	41
4·17	95
3·96	20
3·78	23
3·39	20
3·35	100
3·22	44
3·17	4
3·095	5
2·980	19
2·906	13
2·879	30
2·776	16
2·714	23
2·667	15
2·513	57
2·435	19
2·324	6
2·289	13
2·232	6
2·203	10
2·100	9
2·065	13
2·041	44
2·009	18
1·952	15
1·916	5
1·823	11
1·792	5
1·757	8

TABLE III

Powder data for pentasodium orthoarsenite dodecahydrate, $Na_3H(AsO_3)_2 . 12H_2O$

d(Å)	I	hkl
6·22	15	101
5·65	73	102, 004
4·98	43	103
4·52	43	005, 110
4·27	100	104
4·22	51	112
3·95	34	113
3·76	60	006
3·66	25	105
3·59	14	114
3·25	41	106
3·20	11	007, 200, 115
2·976	14	203
2·888	95	210, 107
2·819	100	008
2·730	34	
2·687	8	213
2·657	6	
2·609	17	205
2·493	25	
2·466	16	
2·424	20	
2·380	7	
2·288	24	
2·263	97	
2·218	20	
2·183	7	
2·159	15	
2·132	3	
2·102	23	
2·050	30	
1·971	7	
1·944	11	
1·875	25	
1·796	25	
1·753	10	

scans are reported in Table IV. Similar remarks apply to the X-ray data of Table V for sodium methoxide which was obtained for comparison. However, the X-ray results were good enough to show that both sodium methoxide and arsenious oxide were not present in the reaction product in major amounts.

TABLE IV

Powder data for the product of the reaction between sodium methoxide and arsenious oxide (Vanzetti's compound)

d(Å)	I
11·5	85
10·0	100
4·98	39
3·30	29
2·85	32
2·27	22
2·16	15
1·91	73
1·87	39

TABLE V

Powder data for sodium methoxide, $NaOCH_3$

d(Å)	I
10·8	60
4·78	20
3·36	20
2·97	50
2·91	30
2·83	80
2·41	100

DISCUSSION

The solid phases stable in the more alkaline region of the sodium arsenite system, as found by different authors, are listed in Table VI.

TABLE VI

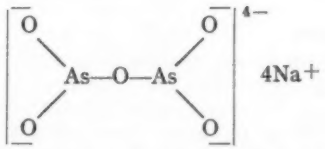
Solid phases in alkaline region of Na_2O-As_2O_3-H_2O system

Present work 25°C	Schreinemakers and de Baat [2] 25°C	Schreinemakers and de Baat modified [3] 25°C	Nelson [3] 35°C
$(NaAsO_2)_x$	$Na_2O.As_2O_3$		$Na_2O.As_2O_3$
$2Na_2O.As_2O_3.8H_2O$		$2Na_2O.As_2O_3.8H_2O$	
	$2Na_2O.As_2O_3.9H_2O$		$2Na_2O.As_2O_3.7H_2O$
$2Na_2O.As_2O_3.11H_2O$		$2Na_2O.As_2O_3.11H_2O$	
$5Na_2O.2As_2O_3.25H_2O$	$5Na_2O.2As_2O_3.26H_2O$		
$2Na_2O.As_2O_3$	$2Na_2O.As_2O_3$		$2Na_2O.As_2O_3$
	$NaOH.H_2O$		$NaOH.H_2O$

Stavenhagen[5] also reported a compound $2Na_2O.As_2O_3.9H_2O$ which he named sodium pyroarsenite. It is possible that this was also a mixture of the two hydrates identified in this work. Although Schreinemakers and de Baat apparently confirm the existence of such a compound, Nelson has shown that their results are more consistent with the existence of two hydrates, as indicated in Table VI. At 25°C the two hydrates have only a very limited range of stability. It is not surprising, therefore, that classical methods of phase study had difficulty in recognising the separate existence of two hydrates in this region. In the present study X-ray analysis easily distinguished two different solid hydrates. Working at 35°C where the compound $2Na_2O.As_2O_3.7H_2O$ is stable over a considerable concentration range, Nelson was able to establish the composition accurately. The water content of the other hydrate is more uncertain but must approximate closely to $2Na_2O.As_2O_3.11H_2O$.

The exact water content of the tetragonal compound, $5Na_2O.2As_2O_3.xH_2O$, is uncertain, but, as indicated below, the most probable value for x is 25.

Structure of arsenites. X-ray structure analysis has shown[1] that sodium polymetaarsenite consists of polymeric anions based on the AsO_3 grouping found in the structure of the polymorphs of arsenious oxide. Making the reasonable assumption that the alkaline arsenites are also based on the AsO_3 structural unit, the structural formula of the most alkaline arsenite, $2Na_2O.As_2O_3$, described in this paper can only be:



This compound is therefore properly designated tetrasodium pyroarsenite.

The tetragonal compound, of empirical formula $Na_{10}As_4O_{11}.25H_2O$ cannot be an acid pyroarsenite or other condensed arsenite since this would require fewer than 8 sodium ions per 4 arsenic atoms. It is therefore an orthoarsenite, $Na_5H(AsO_3)_2.12H_2O$, with two such units per unit cell. A tetragonal arrangement of these atoms and groups is readily visualised. It may be noted here that if Schreinemakers and de Baat's estimate of the water of crystallization is accepted, 25 molecules of water must be distributed within the unit cell. These would be divided into 3 sets, 8 occupying one set of equivalent positions, and 16 occupying a set of more general positions. The remaining water molecule would of necessity have to occupy a very special position in the unit cell, which is unlikely. A statistical distribution of 25 molecules of water over 32 positions is also unlikely. The available evidence therefore points to the compound being pentasodium orthoarsenite dodecahydrate.

According to Stavenhagen[5] the hydrates $2Na_2O.As_2O_3.xH_2O$ are pyroarsenites. However, considering the sequence of solid phases in order of increasing alkalinity: (1) polymetaarsenite, (2) orthoarsenite, (3) pyroarsenite, it would be unexpected if pyroarsenite also appeared between (1) and (2). The compounds $2Na_2O.As_2O_3.xH_2O$ are most likely to be acid orthoarsenites and may be written $Na_2H(AsO_3).(x—1)/2H_2O$ i.e. the trihydrate and pentahydrate of disodium orthoarsenite.

In aqueous solution, therefore, addition of sodium hydroxide to sodium polymetaarsenite causes hydrolysis of the polymeric anions to orthoarsenite. In very alkaline solution, at 25°C, condensation to pyroarsenite occurs before neutralisation of orthoarsenite to trisodium orthoarsenite is complete. At 35°C this condensation

occurs even before the neutralisation reaches the $Na_3H(AsO_3)_2$ stage. Since the phase diagram alters rapidly with temperature it is possible that trisodium orthoarsenite is a stable solid phase at temperatures lower than 25°C.

The evidence that Vanzetti prepared trisodium orthoarsenite is far from convincing. The sodium salts of methyl esters of arsenious acid, and perhaps methyl arsine oxide, are more probable reaction products.

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THE SODIUM ARSENITES
PART III. ACID METAARSENITES*

by

J. W. MENARY

OPSOMMING

Die resultate van 'n voorlopige studie van die sterker suur gedeelte van die Na_2O-As_2O_3-H_2O sisteem word gegee. X-straal-gegewens word vir natrium-suurarseniete en die polimorfe van arseenoksied verskaf. Die chemiese struktuur van hierdie verbindings word bespreek. 'n Tot dusver onbekende natriumarsenaat word beskryf.

SUMMARY

The results of a preliminary study of the more acid region of the Na_2O-As_2O_3-H_2O system are presented. X-ray data are given for sodium acid arsenites and for the polymorphs of arsenious oxide. The structural chemistry of these compounds is discussed. A previously unknown sodium arsenate is described.

INTRODUCTION

Optical measurements on an acid sodium metaarsenite, $NaHAs_2O_4$, have been reported by Flint[1]. No such compound has been found in the Na_2O—As_2O_3—H_2O system at normal temperatures.[2,3]. As pointed out in previous papers in this series[4,5] there is widespread confusion in the literature regarding the identity of various sodium arsenites. The present paper discusses the more acid region of the Na_2O—As_2O_3—H_2O system.

EXPERIMENTAL

The details of the investigation are similar to those described in Part II. In addition to diffractometer studies supplementary X-ray data were obtained with a 57·3 mm diameter X-ray powder camera. Single crystal moving film photographs were taken with a 57·3 mm diameter Weissenberg camera.

RESULTS

Arsenolite. The X-ray powder pattern for arsenious oxide recrystallised from 3N hydrochloric acid was in excellent agreement with A.S.T.M. data and is not therefore reproduced here. The lattice constant of the cubic unit cell was 11·072± 0·002Å in good agreement with the value 11·075Å reported by Swanson and Tatge[6].

Reagent grade arsenious oxide was found to contain a proportion of the monoclinic modification, claudetite I.

Claudetite I. Prolonged heating of arsenolite with a trace of water in a sealed tube at 240°C produced the low temperature modification of claudetite. Recrystallising arsenious oxide from a hot saturated solution in 15% potassium hydroxide provides a more convenient method of preparation. When 15% sodium hydroxide solution was used for recrystallisation a mixture of the cubic and monoclinic polymorphs was obtained.

* A paper read in Pretoria at the Thirteenth Annual Convention of the S.A. Chemical Institute on July 22, 1959.

The powder data reported in Table I were indexed on the basis of a monoclinic cell reported by Buerger.[7] The cell constants were refined except for the interaxial angle β which was accepted as the mean of values reported by other workers.[7,8] Values found were a=5·341±0·008Å (5·25, 5·25), b=12·977±0·004Å (12·87, 12·90), c=4·545±0·006Å (4·54, 4·53), β=93° 51′ (93° 49′, 93° 53′), the figures in parenthesis being values obtained by the earlier workers from single crystal measurements.

Claudetite II. The high temperature modification of claudetite was prepared by heating arsenolite with a trace of water in a sealed tube at 260°C for a period of several weeks. The X-ray powder pattern showed the presence of unchanged arsenolite in the several preparations made. After omitting arsenolite reflections from the powder pattern the remainder of the data could be indexed on the basis of a monoclinic cell of dimensions reported by Becker and his co-workers,[9] (Table II). The cell dimensions were refined in the usual way. Values found for the unit cell parameters, with Becker's results in parenthesis, were: a=8·013±0·008Å (7·99), b=4·561±0·007Å (4·57), c=9·146±0·014Å (9·11), β=101° 34′±6′ (180°—101° 41′).

$Na_2O.3As_2O_3$. In attempting to prepare the compound $Na_2O.3As_2O_3$ reported by Nelson[3], great difficulty was experienced in inducing solutions to crystallise. In the only successful experiment a solution containing 61 g arsenious oxide, 15 g sodium hydroxide and 35 g water was heated at 70°C until a homogeneous syrup was formed. After cooling, the flask was stoppered and the syrup left to crystallise. On long standing two types of crystal separated from the very viscous mother liquor, a few transparent needles and a larger quantity of spherulites. X-ray powder patterns (Tables III and IV) showed that the two materials were different. Analyses of both types of crystal, separated as completely as possible from the mother liquor, were as follows: 13·7% Na_2O, 71·4% As_2O_3 (atomic ratio As: Na=1·6) for the needles, and 19·1%Na_2O, 74·7%As_2O_3 (atomic ratio As : Na=1·2) for the spherulites. A difference in composition is apparent, but because of the difficulty in removing the mother liquor, particularly from the spherulites, and because of the small amount of needle crystals available, the analyses must be considered to be very uncertain.

A zero-level Weissenberg photograph was taken for a small single needle crystal, rotated about the long dimension. The single crystal and the powder data could be interpreted on the basis of a monoclinic unit cell having a=9·12Å, b=14·07Å, c=7·76Å, β=107°.

The spherulitic crystals were not suitable for single crystal examination so that less direct methods of determining the lattice constants were resorted to. The powder data show two series of reflections h00 and 0k0. The derived axial lengths could be used to index all but four reflections. The remainder of the lines were accounted for by choosing a third axis which resulted in a monoclinic unit cell with a=9·15Å, b=14·29Å, c=10·10Å, β=107°.

Technical arsenite of soda. A technical grade arsenite of soda was examined. This material is manufactured from arsenious oxide and sodium carbonate in concentrated aqueous solution from which water is finally expelled by heating at about 100°C. The composition is nominally $As_2O_3.0{\cdot}62Na_2O$.

The X-ray powder pattern was very similar to those in the A.S.T.M. Powder Data File for compounds incorrectly[4] formulated $NaAsO_2$ (card No. 7-9) and Na_2HAsO_3 (card 2-0373). The powder pattern was not that of a mixture of a polymorph of arsenious oxide and sodium polymetaarsenite. Microscopic examination showed that the material was homogeneous, consisting of small tablets showing well-formed pinacoid and prism faces. The crystals were highly birefringent, biaxial, and

they probably belong to the monoclinic system. The density determined by pyknometer was 3·58 g cm^{-3}.

TABLE I

Powder data for claudetite I

d(Å)	I	hkl	d(Å)	I	hkl
6·50	7	020	1·646	1	$17\bar{1}$, 330
4·94	3	110	1·623	2	080, 171
4·11	2	120	1·598	<1	$26\bar{1}$
3·59	4	$10\bar{1}+\beta$	1·576	<1	$33\bar{1}$
3·46	3	$11\bar{1}$	1·552	9	261, 180
3·36	5	130	1·521	<1	$16\bar{2}$, 270
3·25	100	040, 111	1·473	<1	023, $11\bar{3}$, $25\bar{2}$
3·134	1	031, $12\bar{1}$	1·442	1	$12\bar{3}$
2·771	11	140	1·402	<1	$13\bar{3}$, $17\bar{2}$
2·639	2	041	1·392	<1	190
2·608	1	210	1·374	2	091, 351, 360
2·460	<1	220	1·339	<1	$28\bar{1}$
2·333	1	150, 141, $21\bar{1}$	1·310	<1	281, 143
2·256	2	051	1·293	1	$23\bar{3}$, $18\bar{2}$, 332
2·232	1	012,201	1·267	1	290
2·103	1	$15\bar{1}$	1·249	<1	$24\bar{3}$, 342, $37\bar{1}$, 411
2·054	2	240, 151	1·233	<1	421, 440, $29\bar{1}$
2·003	<1	160	1·172	<1	073, $32\bar{3}$, $38\bar{1}$
1·857	3	042, 250	1·167	<1	2. 10. 0
1·786	<1	$14\bar{2}$, $20\bar{2}$	1·142	1	0. 11. 1, $43\bar{2}$
1·751	4	170, $25\bar{1}$	1·060	1	1. 12. 0
1·715	4	071, 320	0·975	<1	1. 10. $\bar{5}$, 541, 0. 13. 1, $32\bar{4}$
1·678	<1	260, $31\bar{1}$	0·966	<1	3. 10. $\bar{2}$, $53\bar{2}$

In view of the similarity in description of technical arsenite of soda and the sodium acid metaarsenite examined by Flint[1], attempts were made to index the powder pattern on the basis of a monoclinic unit cell having axial ratios similar to those given by Flint. The proportionality constant was calculated from the molecular weight, assuming the formula $As_2O_3.0{\cdot}62Na_2O.0{\cdot}38H_2O$, and the measured density of the crystals. With 8 formula weights per unit cell some correspondence was obtained

between the calculated and the observed powder pattern. It was not possible, however, to refine the unit cell parameters, or to account satisfactorily for all the reflections in the powder pattern. Other attempts to index the powder pattern by more general methods were unsuccessful.

TABLE II

Powder data for claudetite II

d(Å)	I	hkl
4·48	100	002
3·93	5	110, 200
3·49	20	111
3·30	16	$20\bar{2}$
2·996	26	003, $10\bar{3}$
2·823	2	112
2·691	8	211, $20\bar{2}$
2·660	8	$30\bar{1}$
2·615	7	103, 300
2·515	7	013, $11\bar{3}$
2·388	3	301
2·238	11	004
2·030	2	022
2·010	4	014, $12\bar{2}$
1·825	18	$10\bar{5}$
1·795	6	005, 204, 303
1·641	4	$30\bar{5}$

TABLE III

Powder data for acid sodium arsenite (needle crystals)

d(Å)	I	hkl
7·19	16	001, 110, 020
4·94	10	101
3·97	3	031
3·59	100	012
3·18	30	041
2·819	2	050
2·688	6	230
2·389	30	*
2·249	2	*
1·910	6	*
1·821	4	*
1·791	26	*
1·731	2	*

*Several alternative indices.

Arsenate impurity in technical arsenite of soda. An unsuccessful attempt to grow single crystals of technical arsenite of soda large enough for single crystal X-ray examination produced a small crop of an isotropic substance from aqueous solution. The crystals showed well-developed octahedral faces and smaller cubic faces. X-ray measurements with single crystals and powder confirmed the cubic symmetry. The powder data of Table V, obtained by diffractometer, gave a value a=19·912Å for the unit cell parameter. Measurements by the Straumanis technique in a 57·3 mm diameter powder camera gave a=19·928Å. The mean value, 19·92Å, is probably accurate to 0·02Å.

Chemical analysis showed that the compound was an arsenate of empirical formula $2Na_2O.As_2O_5{\cdot}22H_2O$ containing 16·1% Na_2O and 32·7% As_2O_5 (theory 16·5% and 30·6% respectively).

TABLE IV

Powder data for acid sodium arsenite (spherulitic crystals)

d(Å)	I	hkl
7·11	1	020
4·84	2	002
4·38	100	200
3·57	17	040
3·40	2	032, 22$\bar{2}$, 13$\bar{2}$
3·36	3	041, 122, 10$\bar{3}$
3·22	2	003, 230
3·160	2	013
3·104	2	132
2·925	44	300
2·383	3	060
2·295	2	160
1·786	2	080
1·753	4	500

TABLE V

Powder data for disodium orthoarsenate hydrate, Na_2HAsO_4, $11H_2O$

d(Å)	I	$h^2+k^2+l^2$	d(Å)	I	$h^2+k^2+l^2$
8·14	18	6	2·144	7	86
7·04	39	8	2·121	15	88
4·98	100	16	2·091	7	91
4·06	80	24	2·073	3	93
3·52	35	32	2·032	6	96
3·25D	22	37, 38	2.015	4	98
3·153	94	40	1·991	7	100
3·089	7	41, 42	1·975	24	102
3·003	6	44	1·939	6	105, 106
2·955	39	45, 46	1·915	9	108
2·875	56	48	1·882	61	113
2·710	71	54	1·870	22	114
2·493	14	64	1·833	6	118
2·462	58	65	1·775	9	126
2·348	29	72	1·707	46	136
3·259	5	78	1·659	40	144
2·228	46	80			

The density of the crystals was found to be 1·949 g cm^{-3} by the density gradient method. The weight of the unit cell contents is therefore 9270 units. Assuming 12 formula weights per unit cell the formula weight predicted by the X-ray data is 773

units. The formula weight is 768 units for $2Na_2O.As_2O_5.23H_2O$. Thus reasonable agreement is obtained with the chemical determination.

Writing the formula in the alternative form, $Na_2HAsO_4.11H_2O$, there are 24 such units in the unit cube.

DISCUSSION

These preliminary results show that these are at least three sodium arsenites more acidic in composition than sodium polymetaarsenite. The known data are summarised in Table VI, in which axes have been modified in some cases to allow for easier comparison.

TABLE VI

Unit cell dimensions for some sodium arsenites

Compound	Molar ratio As/Na	System	a(Å)	b(Å)	c(Å)	α
$(Na\ AsO_2)_x$ (Reference 4)	1·0	O	14·314	6·779	5·086	90°
Spherulites (Table IV)	~1·2	M	14·29	9·15	5·05 x 2	107°
Needles (Table III)	~1·6	M*	14·07	6·80 x 2	5·05 x 2	100°
Technical arsenite of soda	1·62	M(?)				
$NaHAs_2O_4$ (Reference 1)	2·0	M	0·842b	b	0·696b	110° (β)

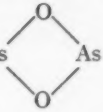
O = orthorhombic M = monoclinic

*Non-primitive unit cell related to that observed experimentally.

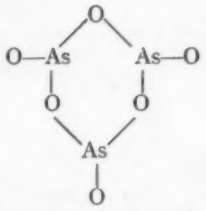
In spite of the uncertainty in the unit cell dimensions of the spherulitic crystals the appearance of similar axial lengths for the different compounds in Table VI must be regarded as being significant. The compounds must therefore have some common structural features. The 7Å spacing common to the powder patterns of the first three compounds in Table VI is a submultiple of the 14Å axis prominent there. This spacing measures the separation of polymetaarsenite chains in the a direction in sodium polymetaarsenite.[4] The separation in the b direction in sodium polymetaarsenite is 6·779Å. A value close to this also occurs in Table VI. Similarly, the repeat distance, 5·086Å, along the polymetaarsenite chain also occurs frequently in the table. It is apparent, therefore, that this group of compounds must have common structural features. The obvious possibility is that they are all polymeric metaarsenites of formula $(Na_yH_{1-y}AsO_2)_x$. If this were the case it would be expected that increase in the acidity would give rise to increased hydrogen bonding between neighbouring chains. The 14Å axis would therefore be expected to shrink with increasing acidity. Table VI shows some evidence that this does occur. On the other hand the repeat distance along the arsenite chain would not be expected to vary appreciably. This is also observed. Distortion of the orthorhombic lattice to monoclinic symmetry could be explained by the sliding of one chain over its neighbours under the influence of hydrogen bonds. More data are required to establish this interpretation with certainty.

Nelson[3] demonstrated the existence at 35°C of a compound which he formulated as $3As_2O_3.Na_2O$. His analytical figures for this compound show more variability than for the other more alkaline arsenites. He assumed an anhydrous compound, but his

data would equally well fit the formula $3As_2O_3.Na_2O{\cdot}2H_2O$, i.e. $(Na_1H_1AsO_3)_x$, an acid polymetaarsenite. However, since he claims that the compound crystallised readily from a limpid solution in contrast to sodium polymetaarsenite which crystallises from a very viscous solution, it is unlikely that a high polymeric compound is involved. The simplest compound having the same relative proportions of arsenic and sodium as $3As_2O_3.Na_2O$ is $NaH_4As_3O_7$. This linear triarsenite contains 14·1% water of constitution which is probably more than can be assumed on the basis of Nelson's experimental work. The presence of



groupings such as are found in claudetite, or other ring structures such as:—



would reduce water of constitution to an acceptable figure. The six-membered ring structure is an attractive possibility because Nelson's compound would then be formulated as $NaH_2As_3O_6$ and technical arsenite of soda has an empirical formula close to $Na_2HAs_3O_6$. Further work is necessary to establish the structure of these compounds with certainty.

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VINNIGE SKEIDINGSMETODES VIR LANTAAN UIT MENGSELS VAN LANTANIEDE*

deur

H. P. MALAN

SUMMARY

Studies concerning the fission products of U-235 made it necessary to develop rapid separation methods for small quantities of lanthanum. The possibilities of procedures based on solvent extraction, anion exchange and cation exchange have been investigated. Procedures are reported by means of which lanthanum can be isolated from mixtures of lanthanides within one hour.

OPSOMMING

Ondersoeke i.v.m. die klowingsprodukte van U-235 het dit nodig gemaak dat vinnige skeidingsmetodes vir klein hoeveelhede lantaan ontwikkel word. Die moontlikhede van prosedures gebaseer op vloeistof-ekstraksie, anioon-uitruiling en katioon-uitruiling is ondersoek. Prosedures word beskryf waardeur lantaan binne een uur uit lantaniede-mengsels geisoleer kan word.

Tydens 'n ondersoek i.v.m. klowingsprodukte met massagetalle 140-143 wat ontstaan wanneer U-235 met termiese-energie neutrone bestraal word, het die behoefte ontstaan aan vinnige skeidingsprosedures vir lantaan uit mengsels van elemente met atoomgetalle tussen 30 en 66 aangesien bestaande prosedures te stadig was vir die doeltreffende isolering van 231 minute La-141, 85 min. La-142 en ~19 minute La-143. Die mees tydrowende gedeelte van die isolering van lantaan uit sulke mengsels bestaan uit die skeiding van die element van die lantaniede en yttrium waarvan die katione, op enkele uitsonderinge na, ook almal 'n lading van +3 dra en baie min in grootte en in elektroniese struktuur van die La^{+3} ioon verskil. Skeidingsprosedures gebaseer op fraksionele kristallisasie[1] en presipitasie[2], op selektiewe reduksie en op papierchromatografie[3] is derhalwe óf ondoeltreffend óf uiters stadig. Kontinueerlike prosesse soos vloeistof-ekstraksie, en ioonuitruiling hou egter die moontlikheid van vinnige skeidingsprosedures in en is gevolglik ondersoek.

1. *Vloeistof-ekstraksie.* Katione van baie elemente vorm met geskikte ligande elektries-neutrale chelaatstrukture[4], sommige waarvan in nie-polêre vloeistowwe oplosbaar is, met die gevolg dat sulke katione uit waterige oplossings geëkstraheer kan word. Die doeltreffendheid van so 'n ekstraksie is afhanklik van die stabiliteit van die chelaat, die oplosbaarheid daarvan in die opponerende fases en dikwels ook van die pH van die waterfase. Die stabiliteit van die chelaat is weer afhanklik van die grootte, die lading en die elektroniese struktuur van die katioon, en van die molekulêre struktuur van die ligand. Enige twee katione kan derhalwe in beginsel deur middel van vloeistof-ekstraksie van mekaar geskei word indien daar 'n verskil in die stabiliteit van hulle onderskeie chelate met 'n bepaalde ligand onder bepaalde kondisies bestaan. Hoe groter die verskil in stabiliteit, des te kleiner is die aantal kontakte tussen opponerende fases wat nodig is om 'n doeltreffende skeiding te bewerkstellig en des te groter die moontlikheid van 'n vinnige skeidingsprosedure.

* 'n Referaat gelewer te Pretoria tydens die Dertiende Jaarlikse Convensie van die S.A. Chemiese Instituut op 22 Julie 1959.

Die grootte van ongehidrateerde trivalente lantaniedekatione (M^{+3}) neem af met toenemende atoomgetal[5], en die stabiliteit van hulle chelate neem derhalwe ooreenkonstig toe[6], sodat vir 'n gegewe sisteem M_{z+1} meer doeltreffend as M_z uit die waterfase onttrek word. Van die verskillende ekstraheermiddels wat ondersoek is, gee alkielfosfate in die algemeen die grootste verskille in die verdelingsverhouding, K, vir aangrensende lantaniede[7, 8, 9]. Maksimum verskille word aangetref by suur oktiel fosfate met vertakte koolstofkettings. In die geval van di-(2-etiel heksiel)-ortofosforsuur, opgelos in tolueen, n-heptaan, ens., as ekstraheermiddel is die waarde van K_{z+1}/K_z sowat 2·5, waar K=lantanied-konsentrasie in die organiese fase/lantanied-konsentrasie in die waterfase[10]. Serium kan maklik van Ce(III) na Ce (IV) geoksideer en dan verwyder word, sodat die isolering van La uit lantaniede mengsels essensieel afhanklik is van 'n doeltreffende La-Pr skeiding. Aangesien di-(2-etiel heksiel)-ortofosforsuur betreklik maklik uit kommersiële oktielfosfaat-mengsels berei kan word[11], en die skeidingsfaktor met hierdie ekstraheermiddel redelik groot is, ($K_{Pr}/K_{La}=\frac{K_{Pr}}{K_{Ce}}\times\frac{K_{Ce}}{K_{La}}=(\sim 2{\cdot}5)^2=\sim 6$), is die moontlikheid van 'n vinnige vloeistofekstraksie-isolering van lantaaan met behulp hiervan ondersoek.

2. *Anioon-uitruiling.* Die lantaniede vorm negatief-gelaaide komplekse met talle ligande soos o.a. chloried[12], tiosianaat[13], etileen-diamientetra-asetaat[6] en die anione van verskeie organiese hidroksisure [14, 15, 16, 17]. Verskille in die stabiliteit van die anioniese komplekse van die verskillende lantaniede met 'n bepaalde ligand kan derhalwe benut word vir skeidingsdoeleindes op 'n anioon-uitruilingskolom. Aangesien die lantaan-komplekse minder stabiel is as die ooreenstemmende komplekse van die swaarder lantaniede en yttrium, word lantaan tydens die elueringstap in so 'n skeidingsprosedure die maklikste van die uitruilingskolom verwyder. Anioon-uitruiling hou derhalwe die moontlikheid van 'n vinnige isolering van lantaan in. Vanweë die skaarste aan kwantitatiewe gegewens i.v.m. die stabiliteit van anioniese lantaniede komplekse is hierdie moontlikheid empiries ondersoek.

3. *Katioon-uitruiling.* Skeidingsprosedures vir lantaniede m.b.v. katioon-uitruilers en geskikte kompleksvormers as eluante is goed bekend[14-22]. Uit die oogpunt van 'n vinnige lantaanskeiding het hulle almal die nadeel dat lantaan heel laaste van die kolom verwyder word. Onlangs is egter daarin geslaag om een van die prosedures[21] sodanige te wysig dat 5-10 mg lantaan in sowat een uur uit lantaniede-mengsels geisoleer kan word[23]. Die mengsels is op 'n Dowex 50 W kolom van 4 mm x 20 cm geadsorbeer en by ~90° met 1·0 M ammonium laktaat (pH=3·32) teen 'n vloeisnelheid van sowat 0·017 ml /minuut geëlueer. Aangesien groter hoeveelhede La gehanteer kan word as in die anioon-uitruilingsprosedure, kan die chemiese opbrengs van die skeidingsprosedure bepaal word deur die lantaan as $La_2(C_2O_4)_3$ te presipiteer, te veras en direk as La_2O_3 te weeg.

EKSPERIMENTEEL

Vloeistof-ekstraksie. Di-(2-etiel heksiel)-ortofosforsuur is berei uit 'n mengsel van oktielfosfate—voorsien deur Victor Chemical Works en bestaande hoofsaaklik uit ongeveer gelyke persentasies van di- en mono- (2-etiel heksiel)-ortofosforsuur, met geringe persentasies van die piro-esters—deur 'n vloeistofekstraksie prosedure met di-etiel-eter en etileenglikol as opponerende fases[10, 11]. Die di-ester is in die eterfase gekonsentreer. Oplossings van verskillende konsentrasies van di-(2-etiel heksiel)-ortofosforsuur in tolueen en in *n*-heptaan is gemaak en as ekstraheermiddels gebruik.

Die verdelingsverhoudings vir lantaan (K_{La}) tussen die organiese fase en die waterfase is bepaal deur gerieflike hoeveelhede 40·2 uur La-140—berei uit 'n (Ba, La)-

140 ewewigsmengsel, verskaf deur Oak Ridge National Laboratory, met behulp van 'n vloeistofekstraksie-prosedure[24]—as radioaktiewe spoorder te voeg by oplossings van $LaCl_3$, van verskillende konsentrasies en by verskillende pH, en die aktiwiteit van gelyke volumes van die opponerende fases, na ekwilibrering, in vooraf-gekalibreerde glasbuise met 'n NaI (Tl) flikkerteller te meet.

Vir pH bepalings is 'n Beckman pH-meter gebruik.

Anioon-uitruiling. Mengsels bevattende La^{+3}, Ce^{+3}, Pr^{+3}, en Y^{+3}, met 40·2 uur La-140, 285 dae Ce-144, 13·8 dae Pr-143 en 58 dae Y-91 as radioaktiewe spoorders—verskaf deur Oak Ridge National Laboratory—is gebruik. Met die oog op doeltreffende skeiding in die kortste moontlike tyd is 'n poreuse anioon-uitruiler (Dowex 1, met 2% oorkruisbinding) met 'n baie klein korrelgrootte (dié wat teen ~1 cm per uur in water uitsak) gekies. Verskillende ligande is uitgetoets en dis gevind dat 'n vinnige lantaanskeiding m.b.v. tiosianaat moontlik is.

Dowex 1 (oorspronklik RC1) is in die tiosianaat vorm verander deur 'n water suspensie daarvan herhaalde male met 2M NH_4SCN te skud. Blootstelling aan die lug het die nat RSCN gou diep-geel laat word, as gevolg waarvan sy uitruilingskapasiteit ernstig benadeel is. Die beste restulate is verkry met varsbereide RSCN wat onder 2M NH_4SCN bewaar is. Hieruit is kolomme met verskillende dimensies berei.

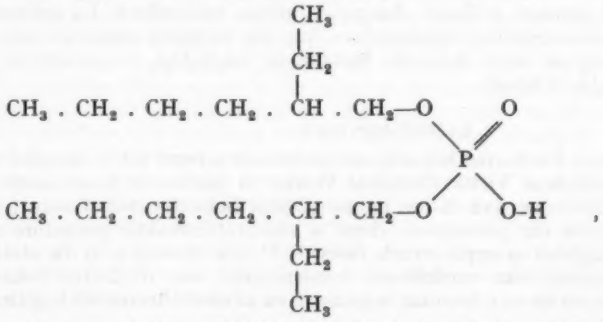
Oplossings van die lantaniedemengsels is drooggedamp en die residu in 2-3 druppels 4M NH_4SCN opgelos teneinde die lantaniede katione in anioniese tiosianaatkomplekse te verander.

$$M^{+3} + 4\ SCN^- \rightleftarrows M(SCN)_4^- \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1)$$

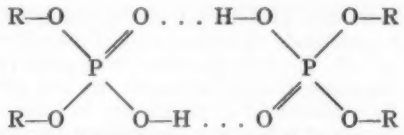
Een druppel 4M NH_4SCN is op die kolom geplaas, gevolg deur die $M(SCN)_4^-$ -oplossing. Hierdeur is die lantaniede as 'n smal band aan die bo-end van die kolom geadsorbeer. Daarna is die mengsel by kamertemperatuur m.b.v. 2M NH_4SCN by verskillende deurvloeisnelhede geëlueer. Elke druppel van die eluaat is opgevang, die aktiwiteit daarvan met 'n sy-venster, metaan-vloei, beta proporsionele teller gemeet, en eluaatkurwes getrek. Die kurwes is ontleed vir die bydrae van elke element deur die aktiwiteit van eluaatfraksies na geskikte tydsverloop weer te bepaal.

RESULTATE EN BESPREKING

Vloeistof-ekstraksie. Di-(2-etiel heksiel)-ortofosforsuur,



(hieronder aangedui deur HA) is 'n taai, bruin vloeistof met S.G. 0·975. Dit is dimeries (ook in organiese oplosmiddels) deur waterstof-binding:



en reageer met M^{+3} deur vorming van 'n 8-ledige chelaat-ring[25,26] as 'n eerste stap:

$$\underset{\text{(org.)}}{3(HA)_2} + \underset{\text{(aq.)}}{M^{+3}} \rightleftarrows \underset{\text{(org.)}}{M(HA_2)_3} + \underset{\text{(aq.)}}{3H^+} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2)$$

$M(HA_2)_3$ is ook oplosbaar in organiese oplosmiddels.

By hoër M^{+3}-konsentrasies en by lae H^+-konsentrasies vind verdere reaksies egter plaas, as gevolg waarvan waterstof in $(HA)_2$ en $M(HA_2)_3$ progressief deur M verplaas word, waarskynlik met vorming van polinukliese reusestrukture, met $(MA_3)_n$ as uiteindelike produk:

$$\frac{n}{2}M(HA_2)_3 + \frac{n}{2}M^{+3} \longrightarrow \underline{(MA_3)_n} + \frac{3n}{2}H^+ \quad .. \quad .. \quad .. \quad .. \quad (3)$$

Die oplosbaarheid van hierdie polinukliese strukture—wit jellieagtige vaste stowwe—in organiese oplosmiddels neem af met toenemende waarde van n.

Uit vgl. (2) volg dat by lae M^{+3}-konsentrasies die konsentrasie van M in die organiese fase, (en dus ook K), omgekeerd eweredig is met die derde mag van H^+-konsentrasie van die waterfase:

$$K = \frac{[M(HA_2)3](org.)}{[M^{+3}](aq.)} = K_{ewewig} \times \frac{[(HA)_2]^3(org.)}{[H]^{+3}(aq.)} \quad .. \quad .. \quad .. \quad .. \quad (4)$$

Aangesien K_{Pr}/L_{La} slegs ~6 is, moet die water-oplossing van die lantaniede-mengsel verskeie kere met vars porsies van die ekstraheermiddel geëkwilibreer word teneinde 'n bevredigende dekontaminasiefaktor te verkry. Soos uit vgls (2) en (4) afgelei kan word, en ook uit Tabelle I en II blyk, word H^+-ione met elke nuwe kontak tussen die opponerende fases vrygestel, sodat die waarde van K_M vinnig afneem met (i) toenemende M^{+3}-konsentrasie en (ii) toenemende aantal kontakte.

TABEL I

Verandering van K_{La} met La^{+3}-konsentrasie

La^{+3}-konsentrasie van waterfase (gm/l.)	5	10	15	20	25
pH van waterfase na ekwilibrering met 'n gelyke volume ekstraheermiddel*	1·22	1·11	1·07	1·03	1·00
K_{La}	6·60	2·50	1·95	1·40	1·05

TABEL II

*Verandering van K_{La} met aantal kontakte tussen $LaCl_3$ opl.** en vars porsies ekstraheermiddel**

Aantal kontakte	1	2	3
pH van waterfase na ekwilibrering met 'n gelyke volume ekstraheermiddel	1·00	0·86	0·78
K_{La}	1·05	0·33	0·17

* 0·75 M $(HA)_2$ oplossing in tolueen.
** 25 gm La per liter.

Uit bepalings soos hierdie het geblyk dat vir 'n vinnige vloeistofekstraksie skeiding van La en Pr d.m.v. genoemde ekstraheermiddel die pH van die waterfase konstant gehou moet word by ~ 1. By hoër pH word 'n te groot persentasie van die La saam met die Pr in die organiese fase geëkstraheer; by laer pH word die aantal kontakte wat nodig is om Pr doeltreffend te ekstraheer te groot. Verskeie pogings om die pH van die waterfase konstant te hou was onsuksesvol. Oordeelkundige verdunning of neutralisering van die waterfase ná elke kontak het geblyk onprakties te wees. Sulfaat-hidrosulfaat buffer kon ook nie gebruik word nie vanweë (i) die geringe oplosbaarheid van $La_2(SO_4)_3$ en (ii) die vorming van anioniese M-sulfaatkomplekse, as gevolg waarvan K_m uiters klein word.

'n Ander aantreklike moontlikheid, nl. om 'n oplossing van die seriumverbinding van $(HA)_2$ in bv. tolueen as ekstraheermiddel in 'n La-Pr skeiding te gebruik, is ook ondersoek. Vanweë die komplekse aard van die reaksie tussen M^{+3} en $(HA)_2$, en die vorming van 'n vaste fase (vgl. 3) was dit egter ook onsuksesvol. Die moontlikheid is blykbaar maar gering om 'n vinnige vloeistofekstraksie skeidingsprosedure vir lantaan uit lantaniede-mengsels te ontwikkel met behulp van di-(2-etiel heksiel)-ortofosforsuur, en waarskynlik nog meer gering met behulp van ander chelateermiddels soos 2-tenoieltrifluoroasetoon[27], difenieltiokarbasoon[28] en 8-hidroksikinolien[29].

Anioon-uitruiling. Uit hierdie ondersoek het geblyk:

(1) dat lantaan altyd eerste aan die onderend van die kolom verskyn,

(2) dat met 2M NH_4SCN as eluant, 'n deurvloeisnelheid van 0·20-0·25 ml./minuut en 'n RSCN kolom van 3 mm x ~ 7 cm die deurbreekpunt 30-40 minute ná die begin van die eluering bereik word,

(3) dat onder hierdie kondisies—vergelyk Fig. 1—

(a) die eluaatkurwes van La en Ce mekaar oorvleuel selfs wanneer draervrye spoorders gebruik word,

(b) die eluaatkurwes van La en Pr mekaar slegs oorvleuel wanneer die mengsel meer as ~ 1 milligram draer-lantaan bevat,

(c) die eluaatkurwes van La en Y mekaar nie oorvleuel nie, en dat

(d) met ~ 1 mg draer-lantaan aanwesig feitlik al die La binne 10 minute ná die deurbreekpunt van die kolom verwyder is.

Lantaan kan dus met behulp van anioon-uitruiling in minder as 'n uur doeltreffend uit lantaniedemengsels geïsoleer word op voorwaarde dat:

(i) Ce vooraf uit sulke mengsels verwyder word,

(ii) die ander lantaniede in draervrye kwantiteite aanwesig is, en

(iii) die hoeveelheid La in die mengsel nie veel meer as ~ 1 mg is nie.

Die serium kan binne enkele minute kwantitatief uit sulke mengsels verwyder word deur dit na Ce (IV) m.b.v. bromaat in suur medium te oksideer en dan met metiel-isobutiel-ketoon[18], 2-tenoiel-trifluoro-asetoon (in xileen[30]) of di-(2-etiel heksiel)-ortofosforsuur (in n-heptaan[24]) te ekstraheer, sodat die hele lantaanskeiding uit lantaniede-mengsels in sowat een uur gedoen kan word.

Fig. 2 toon die eerste gedeelte van die vervalkurwe van die lantaan wat op hierdie wyse geisoleer is uit 1 gram gewone $UO_2(NO_3)_2.6H_2O$-kristalle wat vir 30 minute in 'n termiese energie neutronvloed van ~ 10^{8} neutrone/cm^2/sek. geplaas is. Die aanwesigheid van 231 minute La-141 en 85 minute La-142 daarin is maklik herkenbaar.

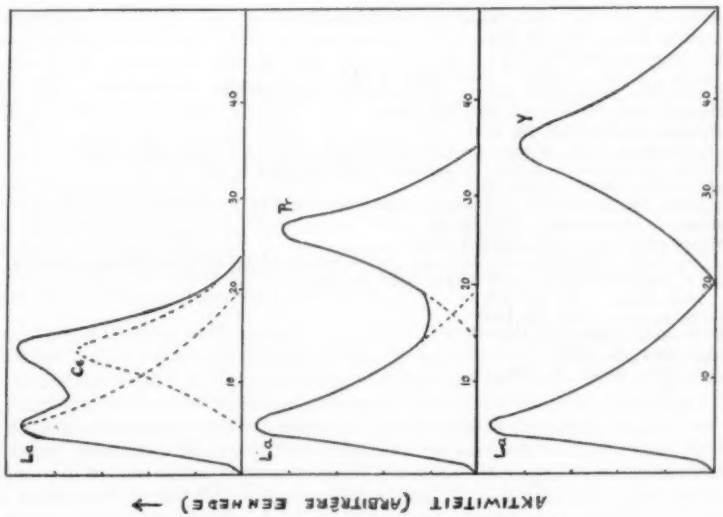


FIG. 1—Elusiekurwes van lantaniede-mengsels bevattende 0·5 mg draer-lantaan.
(Kolom: Dowex 1—x2 in die SCN-vorm, 3 mm x ~7 cm.
Eluant: 2M NH_4SCN
Vloeisnelheid: ~1 druppel per minuut.)

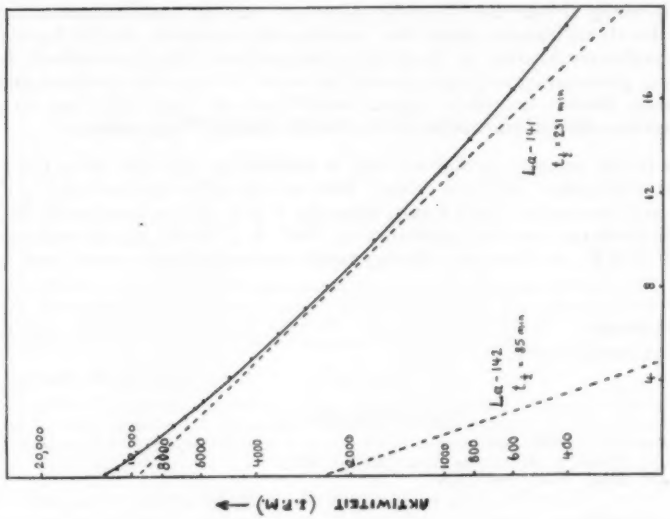


FIG. 2—Vervalkurwe van lantaan geïsoleer uit neutronbestraalde $UO_2(NO_3)_2 . 6H_2O$

Indien dit nodig is om die chemiese opbrengs van die skeidingsprosedure te bepaal, word die eluaatfraksies onder die lantaanpiek versamel, en die La met 'n versadigde oksaalsuuroplossing as $La_2(C_2O_4)_3$ neergeslaan. Die hoeveelheid La is egter te klein om gewoonweg as La_2O_3 geweeg te word. Dit kan wel spektrofometries as die La-Alisarin Rooi S kompleks bepaal word[31], of die $La_2(C_2O_4)_3$ kan op polietileen gemonteer en die La daarin d.m.v. neutronaktivering[32] bepaal word.

Gegewens hierin vermeld is ontleen aan 'n ondersoek uitgevoer deur die skrywer gedurende September 1957 tot Maart 1958 in die radiochemiese laboratorium van Washington Universiteit, Saint Louis, Missouri, V.S.A. Die gewaardeerde belangstelling van die direkteur van die laboratorium, Prof. A. C. Wahl, en die ondersteuning van die W.N.N.R., in die vorm van 'n senior navorsingsbeurs, word met dank erken.

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THE ROUTINE COUNTING OF CARBON—14

by

M. PEISACH

OPSOMMING

'n Verbeterde metode vir die montering van bariumkarbonaat gemerk met koolstof-14 is ontwikkel. Die bariumkarbonaat word oor 'n groot oppervlakte in 'n dun lagie op 'n metaalplaat gesentrifugeer. Die metode maak dit moontlik om monsters maklik en vinnig vir analise voor te berei; die koëffisiënt van variasie van die resultate is kleiner as 2·5%.

SUMMARY

An improved method of mounting carbon-14 labelled barium carbonate is described. Barium carbonate is centrifuged on to a metal plate to produce a thin deposit over a large area. The method permits rapid and easy preparation of samples for analysis; the coefficient of variation of the results is better than 2·5%.

In most tracer work with carbon-14 the labelled sample is ultimately combusted to carbon dioxide which may be analysed as such or precipitated and counted as barium carbonate. This paper deals with a simple procedure for preparing barium carbonate samples by centrifugation.

Most existing methods for mounting carbon-14 labelled barium carbonate for counting purposes depend either on filtration on to paper or some other porous material such as sintered Perspex, or on evaporation of a slurry of the precipitate suspended in some volatile solvent. Although these methods are capable of yielding good results for thick sources, the reported error of 2% is exceeded when thin sources have to be measured. Calvin and others[1] state that "the evaporation (of slurries) is actually a somewhat more complicated process . . . when thin samples have to be made" and Gora and Hickey,[2] who investigated the self-absorption of carbon-14 samples, consider that for very thin samples "it is not possible to spread them out evenly". Winteringham[3] states explicitly that the results obtained from solid counting with internal gas flow counters have an error of $\pm 5\%$. Wick, Barnet and Ackerman[4] stress the need for extreme care in preparing thin samples, and, whilst they do not give any data on their errors, their published curves show a wide scatter of results with thin deposits. It is thus evident that the method described below is of value where the other methods fail, especially for routine analyses when a large number of samples have to be analysed.

In connection with biological work, it frequently happens that samples of low specific activity have to be analysed and usually only a limited weight of material is available. Under such circumstances with existing methods it is necessary to form a thick deposit over a small surface and to correct for the self-absorption of the sample. This self-absorption can be reduced if the sample is deposited in a thinner layer over a larger area with the result that the counting rate will be higher and hence a shorter time will be necessary for counting. To achieve this, precipitated barium carbonate is suspended in alcohol and centrifuged on to a metal plate of large area. Homogeneous reproducible deposits are obtained easily and quickly, especially when thin deposits are prepared. Mention of such a method was made by Calvin *et al.*,[5]

but details of the procedure were not published, and the reproducibility claimed for the method was about the same as for other methods. Evans and Huston[6] used an apparatus similar to the one described below and obtained results with an error of "about 2%". They deposited barium carbonate by warming a suspension of the precipitate in an ether-alcohol mixture and centrifuging it until the solvent evaporated. The method described below is an improvement on the method of Evans and Huston, but does not require centrifugation of warmed mixtures, nor does it involve the grinding of dried barium carbonate.

EXPERIMENTAL

Preparation of barium carbonate. The carbon-14 labelled barium carbonate was precipitated from a sodium carbonate solution in sodium hydroxide by the addition of excess barium chloride in the presence of ammonium chloride equivalent to the free alkali content of the solution. In order to reduce the formation of large crystals the barium chloride was added rapidly as a molar solution at room temperature and a suitable precipitate was obtained when the barium chloride was equivalent to about double the calculated carbonate content of the sample. After precipitation the precipitate was washed three times with water and once with 96% ethyl alcohol. Each time the precipitate was thoroughly dispersed in the wash liquid to obtain an apparently uniform suspension. This was most easily carried out by stirring the mixture to break up the caked solid and thereafter by sucking the coarser lumps into an automatic pipette and expelling it rapidly back into the container with the pipette tip below the level of liquid. In this way a suspension was obtained from which there was no appreciable sedimentation during the first 20-30 seconds. After the alcohol wash the precipitate was suspended in about 20 ml 96% ethyl alcohol and this suspension was used for preparing the mounted sample for counting.

The apparatus. The apparatus for preparing the deposit was a specially prepared centrifuge bucket, the design of which is shown in Fig. 1. It consisted of a metal centrifuge tube, the lower end of which was a flat circular planchet held in position by a base cap screwed up to give a tight seal on a neoprene washer. The outer diameter of the centrifuge metal tube was made to fit the head of a Gallenkamp universal centrifuge, and the diameter of the metal planchet was determined by the diameter of the sample holder of the counter. In earlier experiments, both the bucket and the base cap were made from "Duralumin", but this proved unsatisfactory due to cold welding, or seizure, on the thread of the base cap and corrosion by the wash liquids. Later models were made from stainless steel with nickel-plated brass base caps. The planchets were nickel-plated brass discs about 1·5 mm thick, and the area of the deposit was 19.4 cm^2.

Procedure. With the weighed planchet in position, about 50 ml ethyl alcohol were poured into the bucket and the desired volume of barium carbonate suspension added by transfer pipette. The suspension had to be uniformly dispersed to ensure a good deposit. This was best achieved by the procedure used for washing the precipitated barium carbonate. The suspension could not be mixed by circular movement as this tended to produce a deposit thick at the centre and tapering down to the edge. Rapid injection of the suspension without further treatment tended to concentrate the precipitate at the edges. After transfer, the mixture was centrifuged at 3,000 r.p.m. for 5-10 min. The supernatant liquid was then sucked off and the deposit dried by an infra-red lamp. Thereafter the planchet was removed, oven-dried at 120°C and weighed. The samples were counted in an NMC proportional counter converter, which is a windowless gas flow proportional counter operated at atmospheric

pressure with "Tracerlab" proportional gas, a mixture of about 10% methane and 90% argon.

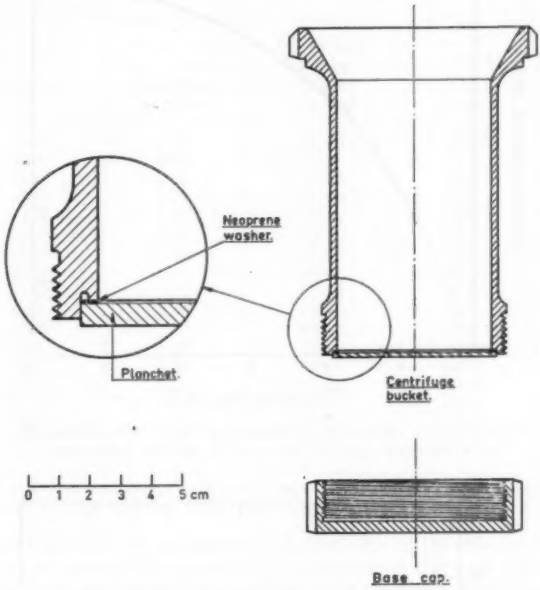

FIG. 1—Centrifuge bucket with base cap showing design of the bottom of the bucket where the washer is placed

RESULTS

A test series of 71 analyses was carried out. The results are shown in Figs. 2 and 3 and some are listed in Table I. In the former curve the activity is plotted against the thickness of the deposit, whilst the latter shows the same results plotted against the percentage transmission, R, where (100-R) represents the percentage loss of activity due to self-absorption and possibly other causes. The form of the curve in Fig. 3 corresponds to the well-known self-absorption expression

$$R=\frac{100\ (1-e^{-\mu s})}{\mu s}$$

where s is the thickness of the deposit in mg/cm^2 and μ the mass absorption coefficient which, in this case, was found to have the value 0·55 cm^2/mg and is in good agreement with published values[7] for windowless counters.

A statistical analysis of the results showed that the coefficient of variation, v, of the corrected specific activity of a sample, $\bar{a}$, has the value 2·4(2)% over the range of thicknesses from 1 to about 6 mg/cm^2

$$\text{where } v=\frac{100\sigma}{\bar{a}}$$

σ is the standard deviation and $\bar{a}$, the mean specific activity.

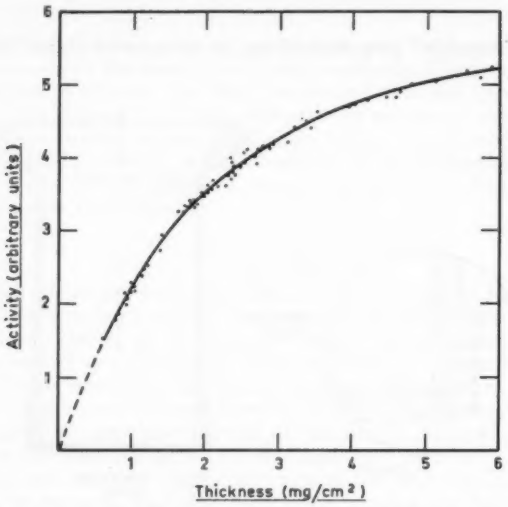

FIG. 2—The variation of obtained activity with thickness for a constant specific activity of barium carbonate

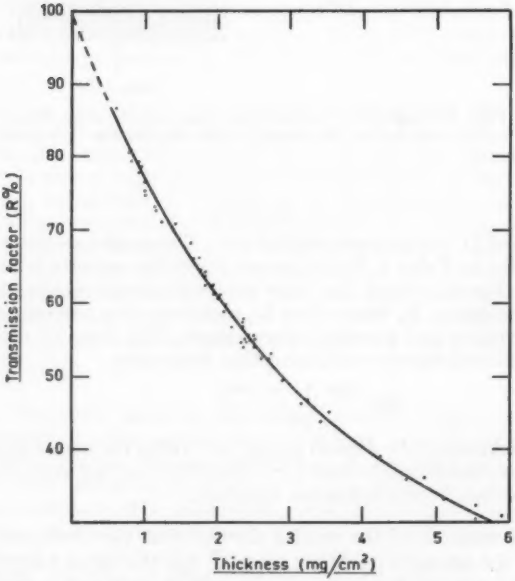

FIG. 3—The variation of the percentage transmission with thickness. Points are experimental values whilst the line shows the calculated values obtained from

$$R = \frac{100(1-e^{-\mu s})}{\mu s} \text{ with } \mu = 0{\cdot}55$$

TABLE I

Some values obtained for thin deposits of $BaCO_3$

No.	$BaCO_3$ mg	Thickness mg/cm²	Corrected Specific Activity c/m/mg	R Exptl.	R Calculated
55	14·9	0·77	14·78	80·3	81·6
54	18·1	0·93	15·07	78·5	78·2
46	19·6	1·01	14·95	76·3	76·7
41	23·0	1·19	14·90	72·7	73·5
19	34·3	1·77	15·12	64·3	64·0
13	35·5	1·83	14·90	62·5	63·0
4	35·7	1·84	15·23	63·7	62·9
20	38·0	1·96	15·01	61·2	61·2
3	39·2	2·02	15·14	60·9	60·4
8	46·1	2·38	15·09	55·1	55·8
10	46·6	2·40	14·87	55·0	55·5
23	47·1	2·43	15·00	55·1	55·2
24	52·1	2·69	14·97	52·1	52·2
33	62·6	3·23	15·03	46·8	46·8
61	82·2	4·24	15·14	38·9	38·7
70	99·8	5·14	15·19	33·6	33·3
70	111·5	5·75	14·70	30·2	31·6

For the series of 71 analyses, the mean corrected specific activity was 14·96 c/m/mg with a standard deviation of 0·36; *i.e.* coefficient of variation v=2·4%.

In addition to the series of analyses mentioned above, this method has been used in our Laboratories for several thousands of analyses over the past four years. During that time the method was tested repeatedly and analyses were carried out with deposits thinner than 1 mg/cm² and thicker than 6 mg/cm². The thinner samples were prepared with great ease and the results were within the stated limits of precision, but thick deposits tended to crack on drying and to break at the edges when removed from the centrifuge bucket. Accordingly, this method is not recommended for thick deposits.

The author wishes to thank Mr. I. Roth for assistance during the development stages and Mrs. A. Slaa and Mrs. M. M. Pols for assistance with the analyses.

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Pretoria.

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A GLOW DISCHARGE DETECTOR FOR GAS CHROMATOGRAPHY

by

R. A. BASSON, C. R. DE WET,* W. NEL and V. PRETORIUS

OPSOMMING

Die toestande waaronder maksimum gevoeligheid en stabiliteit verkry word by 'n gloedontladingsdetektor is ondersoek. Parameters wat 'n belangrike rol speel is die aangelegde spanning, die elektrodemateriaal en die tipe draergas.

SUMMARY

The conditions under which maximum sensitivity and stability are obtained from a glow discharge detector have been investigated. Parameters which play an important role are the applied voltage, the electrode material and the nature of carrier gas.

It has been shown[1] that the voltage drop across a low pressure glow is strongly affected by the presence of small quantities of impurity in the gas between the electrodes, and that this principle may be employed as the basis of a highly sensitive detector for gas chromatography[2]. Modified neon lamps have recently been used for this purpose[3] but appear to be limited to the detection of hydrocarbon vapours, since the electrode material is affected by oxidising compounds. The performance of a glow discharge detector is strongly affected by a number of parameters including the electrode material, the distance between the electrodes, the gas pressure in the glow, the applied voltage, etc. The purpose of the present investigation was to study the conditions under which maximum sensitivity and stability are obtained from a glow discharge detector.

The general characteristics of low pressure gas discharges. A schematic representation of the current-voltage characteristic of a self-sustaining gas discharge is shown in Fig. 1[4]. The voltage has been plotted on a linear and the current on a logarithmic scale.

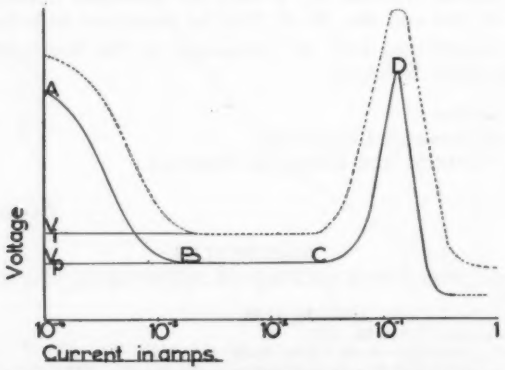

FIG. 1—A schematic representation of the current-voltage characteristics of a self sustaining Gas discharge

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The value of the voltage drop across the electrodes is changed by changing the composition of the gas between the electrodes. Although precise data are lacking, the voltage-current curve of an impure gas may be schematically represented by the dotted curve in Fig. 1. The voltages V_i and V_p are characteristic of the impure and pure gases respectively and are not affected by changes in the current, due to fluctuations in the applied voltage, within the range BC. The potential change (V_i-V_p) is, therefore, a function of the composition of the gas. As an illustration of the sensitivity of this method of detecting changes in the composition of a gas, it may be mentioned that the presence of as little as 0·1% of air in neon produces a voltage change of approximately 150 mV across the electrodes[5].

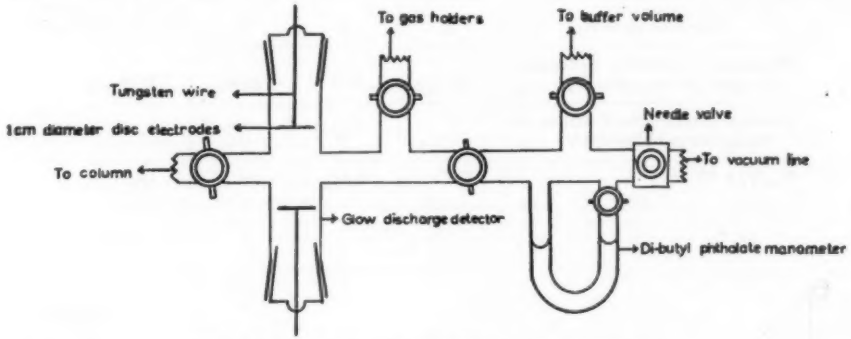

FIG. 2—Schematic representation of the apparatus

EXPERIMENTAL

A schematic diagram of the apparatus is shown in Fig. 2. An electronically controlled power supply delivering 700 volts was used as voltage source. The noise of the electrical system in the absence of the glow discharge was less than 2·5 mV. The potential drop across the electrodes was measured by means of a vacuum tube voltmeter (Philips GM6008).

RESULTS

The current voltage characteristics of the detector with various common carrier gases were determined at a series of gas pressures and electrode separations using nickel electrodes. The results are shown in Figs. 3, 4 and 5. A similar series of curves was obtained using platinum, iron, aluminium and copper electrodes. These differ from the curves in Figs. 3, 4 and 5 with respect to the striking and running voltages only and are consequently not reproduced here. From these results (i.e. taking Figs. 3, 4 and 5 in conjunction) it may be concluded that at an electrode separation of less that 1 cm, a running current of about 1 mA, and a pressure of 3 to 6 mm Hg the detector shows a minimum sensitivity to fluctuations in pressure and current. Furthermore, if the above conditions are satisfied a glow discharge with normal cathode fall is obtained.

The effects of the following parameters on the sensitivity (i.e. the maximum voltmeter deflection per unit volume of sample injected) and on the stability (i.e. the average random voltage fluctuations) were investigated. In each case 1 microlitre samples of ether were injected into a stream of carrier gas which was then swept through the chromatography column. The column was so packed that, with a pressure

of 1·1 atmospheres at the inlet side and the needle valve fully open, the pressure in the detector was 1·8 mm Hg. The results are shown in Table I.

Pressure

TABLE I

The effect of pressure on sensitivity and stability

Temperature: 18°C
Carrier gas: Argon
Applied potential: 300 volts
Flow rate: 2 cm/sec (linear)
Electrode material: Platinum

Pressure (mm Hg)	2	3	8	12
Maximum voltmeter deflection in volts per μl. ether V_m	20·1	20·6	21·0	21·3
Average random fluctuations of voltmeter in millivolts V_f	7	8	10	15
$V_m/V_f \times 10^{-3}$	2·87	2·57	2·1	1·42

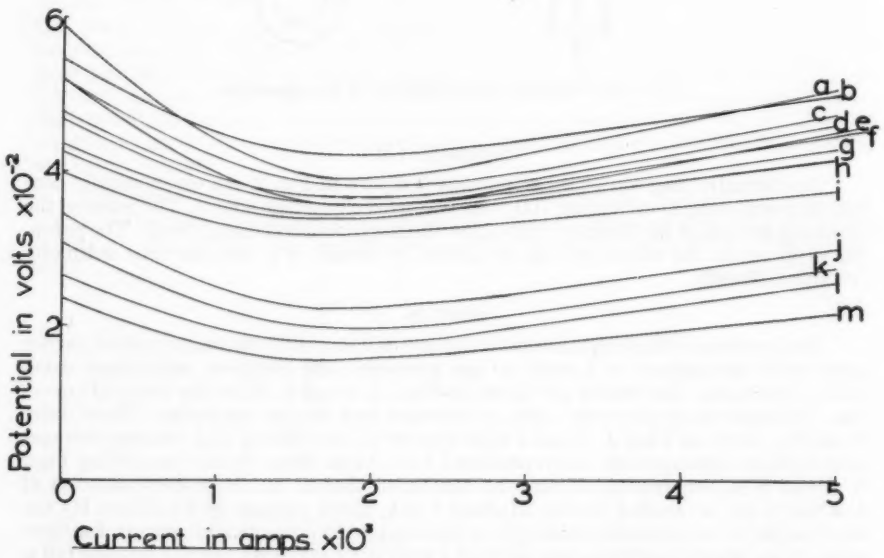

FIG. 3—The effect of electrode separation on the current-voltage characteristics of hydrogen, oxygen, nitrogen and argon between nickel electrodes at a pressure of 3 mm mercury

A Oxygen 2cm
B Nitrogen 2 cm
C Hydrogen 2 cm
D Nitrogen 1 cm
E Oxygen 1 cm
F Hydrogen 1·5 cm
G Nitrogen 0·5 cm
H Hydrogen 10 cm
I Hydrogen 0·5 cm
J Argon 2 cm
K Argon 1·5 cm
L Argon 1·0 cm
M Argon 0·5 cm

From the results in Table I it is apparent that the value of the maximum voltage deflection V_m is not noticeably affected by the pressure but that the average random voltage fluctuations V_f increase as the pressure is increased, and consequently V_m/V_f is correspondingly decreased, although it remains roughly constant in the region 2-6 mm Hg.

Applied voltage

TABLE II

The effect of the applied voltage on sensitivity and stability

Temperature: 18°C
Carrier gas: Argon
Electrodes: Platinum

Flow rate: 2 cm/sec (linear)
Pressure: 3 mm Hg

Applied Voltage (volts)	300	400	500	600
Maximum voltmeter deflection (in volts) per μl. ether V_m	19·6	20·1	20·6	21·0
Average random fluctuations of voltmeter in millivolts V_f	8	15	28	40
$V_m/V_f \times 10^{-3}$	2·45	1·34	·74	·52

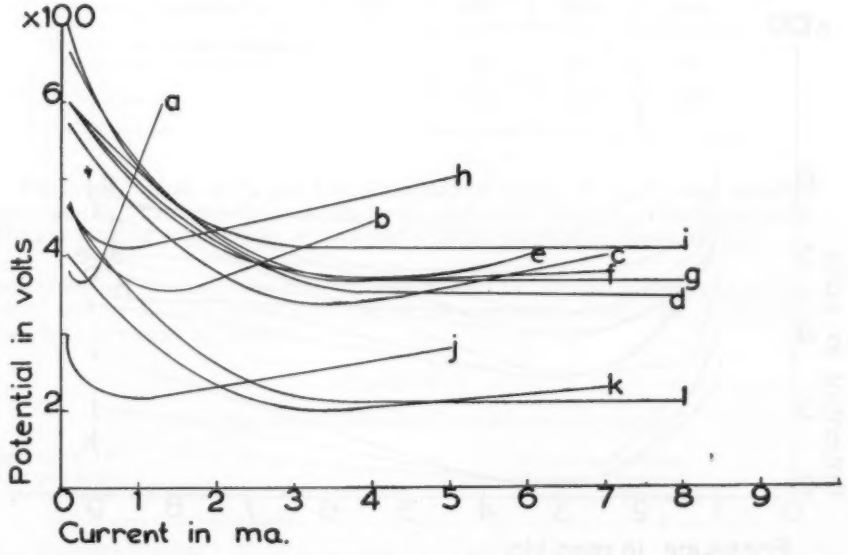

FIG. 4—The effect of pressure on the current-voltage characteristics of hydrogen, nitrogen, oxygen and argon between nickel electrodes 1 cm apart

A 1 mm Hydrogen	E 3 mm Oxygen	I 9 mm Nitrogen
B 3 mm Hydrogen	F 6 mm Oxygen	J 3 mm Argon
C 6 mm Hydrogen	G 9 mm Oxygen	K 6 mm Argon
D 12 mm Hydrogen	H 3 mm Nitrogen	L 9 mm Argon

From Table II it is evident that the detector is best operated at the minimum applied voltage necessary to sustain the glow. The increase in V_f with an increase in the applied voltage may be ascribed to sputtering and to the increase in the current density which leads to an abnormal glow.

Electrode material

TABLE III

The effect of the electrode material on sensitivity and stability

Temperature: 18°C
Carrier gas: Argon
Applied potential: 300 volts

Flow rate: 2 cm/sec (linear)
Pressure: 2·8 mm Hg

Electrode Material	Platinum	Iron*	Nickel	Aluminium	Copper
Maximum voltmeter deflection in volts per μl. ether V_m	20	22	25	13	15
Average random fluctuations of voltmeter in millivolts V_f	6	8	17	30	35
$V_m/V_f \times 10^{-3}$	3·33	2·75	1·47	·43	·43

*Bright steel

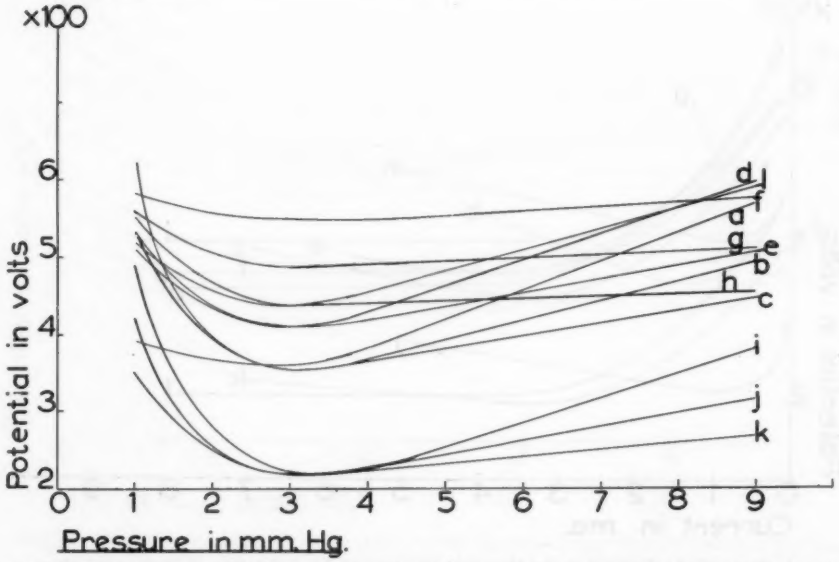

FIG. 5—Variation of potential difference with pressure at constant voltage using Ni-electrodes 1 cm apart

A	Hydrogen 0·5 mA	E	Nitrogen 1·0 mA	H	Oxygen 1·5 mA
B	Hydrogen 1·0 mA	L	Nitrogen 1·5 mA	I	Argon 0·5 mA
C	Hydrogen 1·5 mA	F	Oxygen 0·5 mA	J	Argon 1·0 mA
D	Nitrogen 0·5 mA	G	Oxygen 1·0 mA	K	Argon 1·5 mA

The values of V_f in Table III were obtained using clean electrode surfaces. After repeated use the value of V_f for platinum remained virtually unchanged but in the case of the other electrodes, particularly of aluminium and copper, V_f increased markedly. These results can be interpreted as being due to reactions between oxygen-containing molecules and the electrode material. When hydrocarbons were passed through the detector the values of V_f were found to be somewhat less than those given in Table III. This is in agreement with the results obtained by Pitkethly[3].

For general analytical work it may be concluded that chemically inert electrodes such as platinum should be used.

Nature of carrier gas

TABLE IV

The effect of the carrier gas on sensitivity and stability

Temperature: 18°C
Applied potential: 300 volts
Flow rate: 2 cm/sec (linear)

Pressure: 2 mm Hg
Electrodes: Platinum

Gas	Argon	Nitrogen	Hydrogen	Oxygen
Maximum voltmeter deflection in volts per μl ether V_m	20·1	20·1	20·0	20·0
Average random fluctuations of voltmeter in millivolts V_f	7	20	20	30
$V_m/V_f \times 10^{-3}$	2·9	1·00	1·00	0·67

The lowest values of V_f and hence the highest values of V_m/V_f were obtained using argon as a carrier gas as is shown by the results in Table IV. This is due partly to the low striking voltage (Fig. 3), and partly to the chemical inertness of argon.

Temperature and flow rate. The detector is unaffected by changes in temperature from 15-88°C and by changes in the flow rate of the carrier gas from 1-2·5 cm/sec as is shown by the results in Table V.

TABLE V

The effects of flow rate and temperature on sensitivity and stability

Temperature: 18°C
Carrier gas: Argon
Applied potential: 300 volts

Flow rate: 2 cm/sec
Pressure: 2 mm Hg
Electrodes: Platinum

Flow rate in cm/sec	1·0	1·5	2·0	2·5
V_m/V_f	2·7	2·6	2·9	2·8
Temperature	15°C	30°C	60°C	88°C
V_m/V_f	2·8	2·7	2·8	2·6

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A FLAME-IONISATION DETECTOR FOR GAS CHROMATOGRAPHY. THE EFFECT OF A NUMBER OF PARAMETERS ON THE SENSITIVITY

by

R. R. ARNDT,* W. J. NEL AND V. PRETORIUS

OPSOMMING

'n Studie is gemaak van die invloed van 'n aantal parameters op die sensitiwiteit van 'n vlamionisasiedetektor vir gaschromatografie.

SUMMARY

The effects of a number of parameters on the sensitivity of a flame ionization detector for gas chromatography are described.

A brief description of a flame-ionisation detector for gas chromatography has recently been given.[1,2] The detector works on the principle that a measurable ion-current is produced in an oxy-hydrogen flame, and that this current is changed by the presence of organic vapours eluted from a gas chromatography column, the change being proportional to the amount of the organic vapour. This detector has been successfully used in these Laboratories during the past year. It is particularly suited to the analysis of high-boiling compounds since it is constructed entirely from glass and metal and can therefore be heated to high temperatures. The effects of a number of parameters on the sensitivity of the detector are described in the present paper.

EXPERIMENTAL

A schematic diagram of the detector is shown in Fig. 1. The gases eluted from the column were mixed with hydrogen and burnt at the tip of a glass jet in the presence of sufficient oxygen to support the combustion. Precision regulators and rotameters were used to control and measure the gas flow rates.

The two electrodes between which the ion-current was measured consisted of platinum discs brazed onto brass rods which were threaded into brass plugs. This arrangement allowed the distance between the electrodes to be changed.

A close-fitting glass sleeve permitted the distance of the electrodes above the tip of the jet to be adjusted. Condensed water vapour, which formed during the combustion, was prevented from running back on to the electrodes by a rim.

The ion-current between the electrodes was measured by means of the circuit shown in Fig. 2. Basically the circuit consisted of a balanced cathode follower impedance transformer with a 0-500 mV recording potentiometer connected across the output terminals. A voltage of up to approximately 200 volts could be applied across the electrodes without damaging the tube.

The sensitivity of the detector was determined by injecting 5μl. samples of a solution containing 1% xylene in benzene and measuring the height of the xylene peak in the chromatogram.

* National Chemical Research Laboratory, Council for Scientific and Industrial Research, Pretoria.

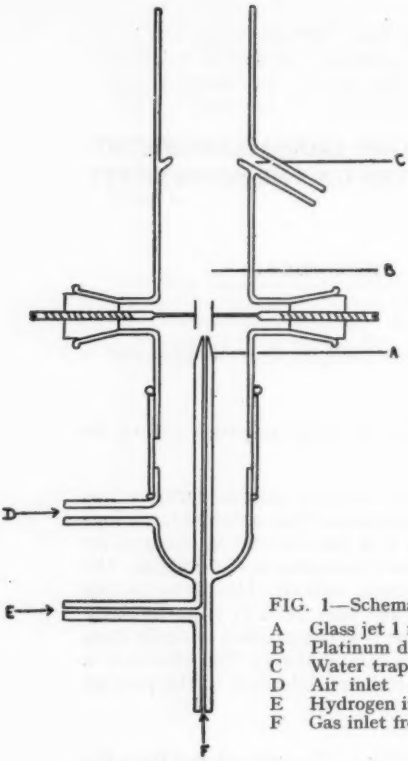

FIG. 1—Schematic diagram of detector

A Glass jet 1 mm I.D.
B Platinum disc electrodes 1 cm diameter
C Water trap
D Air inlet
E Hydrogen inlet
F Gas inlet from column

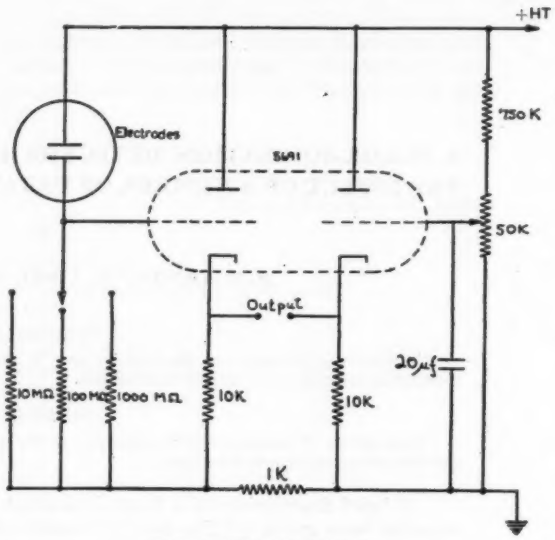

FIG. 2—Electrical circuit

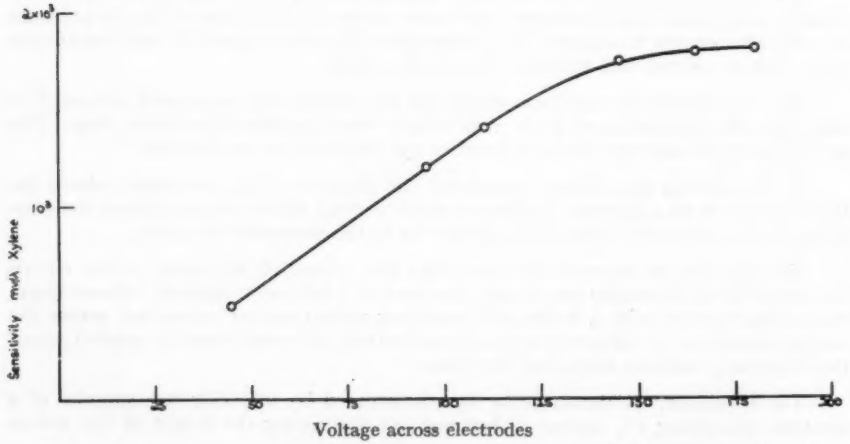

FIG. 3—The effect of the voltage across the electrodes on the sensitivity
Distance between electrodes 6 mm
Distance of electrodes above jet tip 3 mm
Hydrogen flow rate 35 ml/min

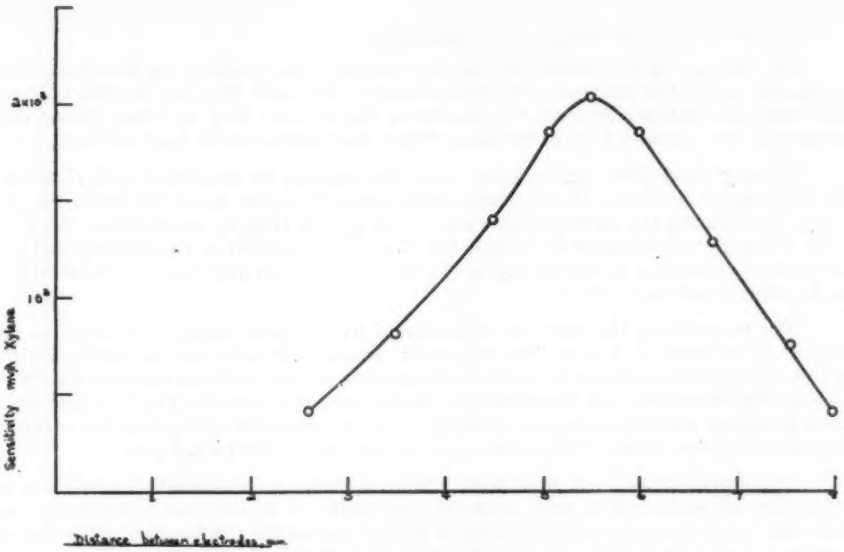

FIG. 4—The effect of the distance between the electrodes on the sensitivity
Voltage across electrodes 180 volts
Distance between jet tip and electrodes 2mm
Hydrogen flow rate 35 ml/min

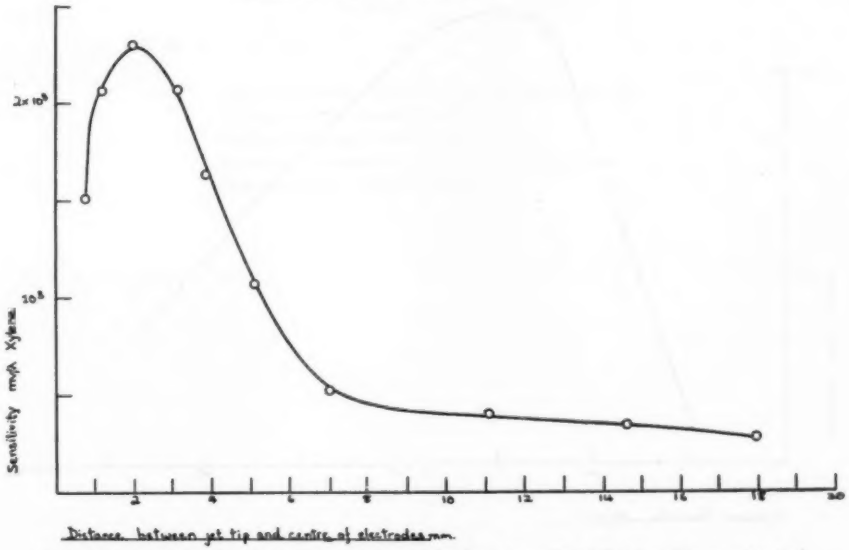

FIG. 5—The effect of the distance of the electrodes above the jet tip on the sensitivity
Voltage across electrodes 180 volts
Distance between electrodes 5.5 mm
Hydrogen flow rate 35 ml/min

RESULTS

An increase in the sensitivity of the detector was obtained by increasing the potential across the electrodes to approximately 180 volts (Fig. 3). At this voltage the optimum distance between the electrodes was 5·5 mm (Fig. 4) which placed the electrodes on the outer edge of the flame where the combustion is most efficient.

Having fixed these parameters, a further increase in sensitivity was obtained by placing the centres of the electrodes approximately 2 mm above the tip of the jet (Fig. 5) and using the hydrogen flow rate of 28 ml/min (Fig. 6). In each case the flow rate of the air was adjusted to provide the theoretical amount of oxygen required for complete combustion of the hydrogen. A slight excess of air was however required for maximum sensitivity (Fig. 7).

The response of the detector as measured by the peak height was found to be linear up to 0·05 μl. xylene. The minimum amount of butyl alcohol diluted with methyl alcohol which could be detected at the highest sensitivity setting was 6×10^{-11} moles. This deflection was five times the background fluctuations. The base-line drift was less than 1·0 mV/h and was unaffected by considerable changes in the column temperature and by small fluctuations in the flow rate of the carrier gas.

The detector has been used with a wide variety of compounds. Calculation is necessary for quantitative work since the sensitivity of the detector is dependent on the number of charged carbon aggregates formed during the combustion of the eluted solute.[3]

A typical chromatogram obtained with this detector is shown in Fig. 8.

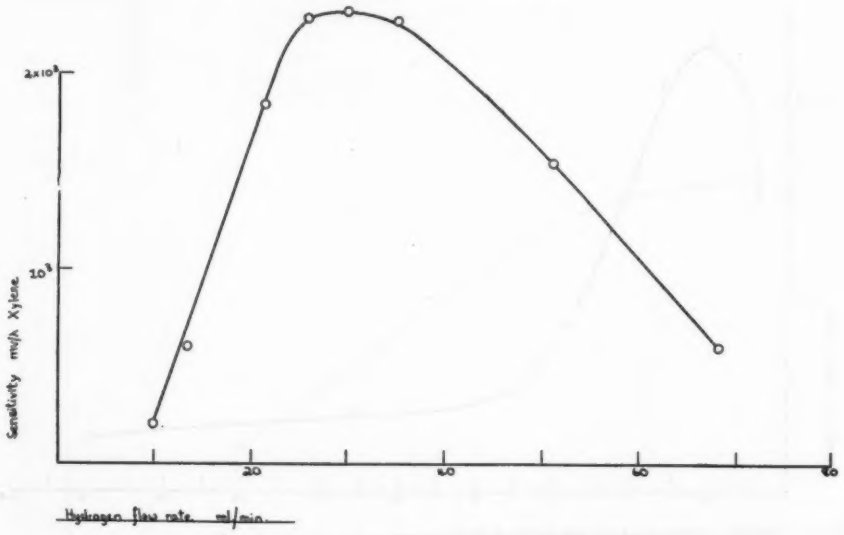

FIG. 6—The effect of the hydrogen flow rate on the sensitivity
Voltage across electrodes 180 volts
Distance between electrodes 5.5 mm
Distance between jet tip and electrodes 2 mm

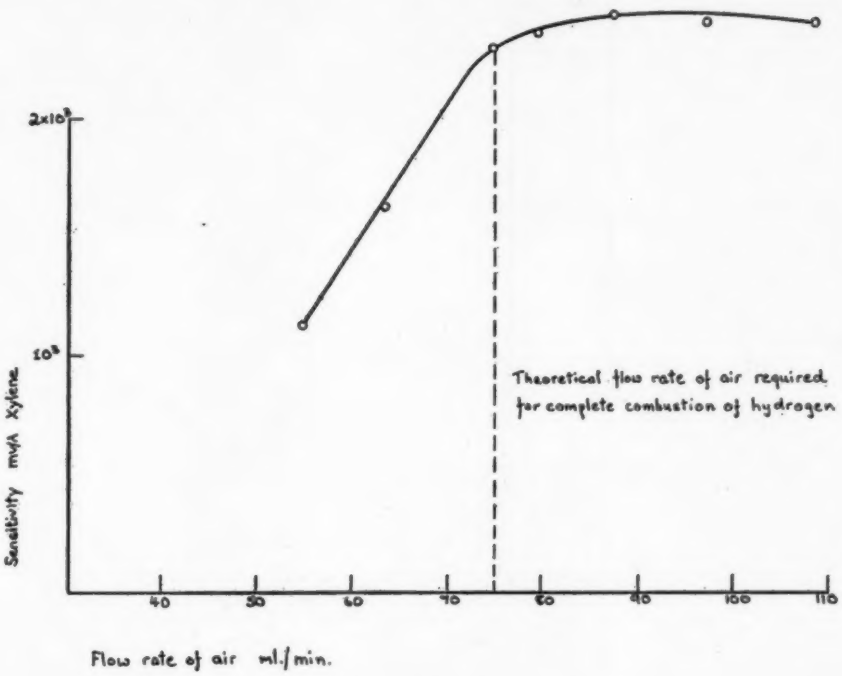

FIG. 7—The effect of the air flow rate on the sensitivity
Voltage across electrodes 180 volts
Distance between electrodes 5.5 mm
Distance between jet tip and electrodes 2 mm
Hydrogen flow rate 30 ml/min

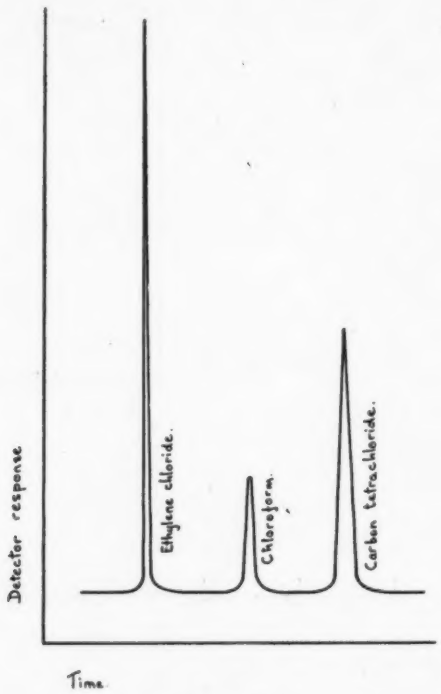

FIG. 8—Typical chromatogram

One of us (R.R.A.) wishes to thank the South African Council for Scientific and Industrial Research for the permission to participate in this work, and the other (V.P.) is indebted to Messrs. African Explosives and Chemical Industries, Limited, for the award of a Research Fellowship.

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A SPECTROGRAPHIC METHOD FOR THE ANALYSIS OF PLANT MATERIAL USING SODIUM PYRROLIDINEDITHIOCARBAMATE FOR THE CONCENTRATION OF THE TRACE ELEMENTS

by

A. STRASHEIM, D. J. EVE and R. M. FOURIE*

OPSOMMING

'n Chemiese metode vir die konsentrasie van spoorelemente met gebruik van natrium pirrolidienditiokarbamaat, is deur Stetter en Exler voorgestel. Hierdie metode is getoets vir die ontleding van plantmateriaal vir Pb, V, Mo, Mn, Zn, Co en Ni. Tin is as interne standaard gebruik. Die invloed van verandering in ysterinhoud op die ontleding is bestudeer.

SUMMARY

A chemical method for the concentration of trace elements using sodium pyrrolidinedithiocarbamate has been suggested by Stetter and Exler. This method has been tested for the analysis of plant materials for Pb, V, Mo, Mn, Zn, Co and Ni. Tin was used as internal standard. The influence of variation in the iron content on the analysis has been assessed.

INTRODUCTION

A rapid method for the concentration of trace elements using sodium pyrrolidinedithiocarbamate[1] has been published by Stetter and Exler[2]. It has successfully been applied in the analysis of plant materials by Scharrer and Judel,[3] using iron as internal standard. This, however, requires that the iron be present in constant concentration in all the analytical samples. It is therefore necessary to analyse for the iron chemically and to add the required amount.

The use of only one extraction to separate the trace elements from the major consistuents of plant material is a very attractive feature of this method. Its possibilities using an added internal standard are reported in this paper.

EXPERIMENTAL

Preparation of samples. Piper's[4] method of ashing was used. After dry ashing a 10 g sample at 430-450°C for 16-18 hours, the ash was dissolved with hydrochloric acid, the silica filtered off and treated with hydrofluoric and sulphuric acids. The residue was then dissolved in hydrochloric acid and added to the filtrate. The concentration procedure suggested by Stetter and Exler was then used. After addition of sulphosalicylic acid and adjustment to pH 4·8 with ammonium hydroxide, the heavy metals were precipitated by the addition of sodium pyrrolidinedithiocarbamate. Chloroform was added to dissolve the metal complexes and the organic phase separated. The chloroform extract was then evaporated to small volume and 0·09 g of graphite containing 1 mg of tin as internal standard, added. The extract was dried, heated to 450°C for about 30 minutes and then mixed with 30 mg of lithium carbonate. This was sufficient to fill three electrodes.

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Spectrographic conditions and apparatus.

Excitation:	10 amps D.C. from a constant current source[5] (sample anode).
Spectrograph:	Large Hilger Prism. The wavelength range 2550Å to 3850Å was used.
Microphotometer:	Optica Milano.
Exposure:	Samples burnt to completion—approximately 2·5 minutes. Each sample was arced in triplicate and the mean taken.
Electrodes:	Standard undercut carbon cathode and a 2 mm diameter 8 mm deep sample-carrying electrode[6].
Plates:	Ilford Thin Film Halftone.

The other conditions were the same as those used by Strasheim and Camerer[7].

Analysis lines. The following element lines were used for the analyses:

Pb	2833·1 Å
V	3185·4 Å
Mo	3170·3 Å
Mn	3044·6 Å
Zn	3345·0 Å
Co	3044·0 and 3453·5 Å
Ni	3050·8 Å
Sn	3032·8 Å (internal standard)

Internal standard. A relatively large amount of tin (1 mg) was added to the samples to avoid interference from the small concentrations of tin occurring in plant materials. (Alternatively palladium may be used as internal standard. In this case 0·1 mg of palladium is added and the Pd 3027·9 Å line used). Addition of tin solution to the sample solution before extraction was found to be unsatisfactory due to the instability of the tin solution. For this reason stannic oxide was used with the graphite base.

Influence of iron concentration on standard curves. Standards were prepared in a graphite base containing 3-1000 p.p.m. of lead, vanadium, molybdenum, cobalt and nickel and 30-10,000 p.p.m. of zinc and manganese. One part of lithium carbonate was added to three parts of the standard mixtures before burning. To obtain standard analysis curves, three electrodes of each standard were burnt, the averages plotted and the best straight line drawn.

As iron formed a major part of the trace element precipitate, it was necessary to assess the influence of variation in its concentration on the determination of the other elements. Three series of standards were therefore prepared in which the iron concentrations were 10%, 5% and 0%.

The intensity ratios, when plotted against concentration on logarithmic paper, gave parallel curves, as illustrated in Fig. 1 for lead, nickel and molybdenum. The separation of these curves was different for each element and showed that, for a particular intensity ratio, an error of from 5 to 40% could be incurred. It was found possible to overcome this difficulty by using the Fe 2990·39 Å line to obtain a measure of the iron concentration. The correct element concentration was then determined from a standard curve interpolated for this iron concentration. The same internal standard line was used for the iron determination. No background correction was made.

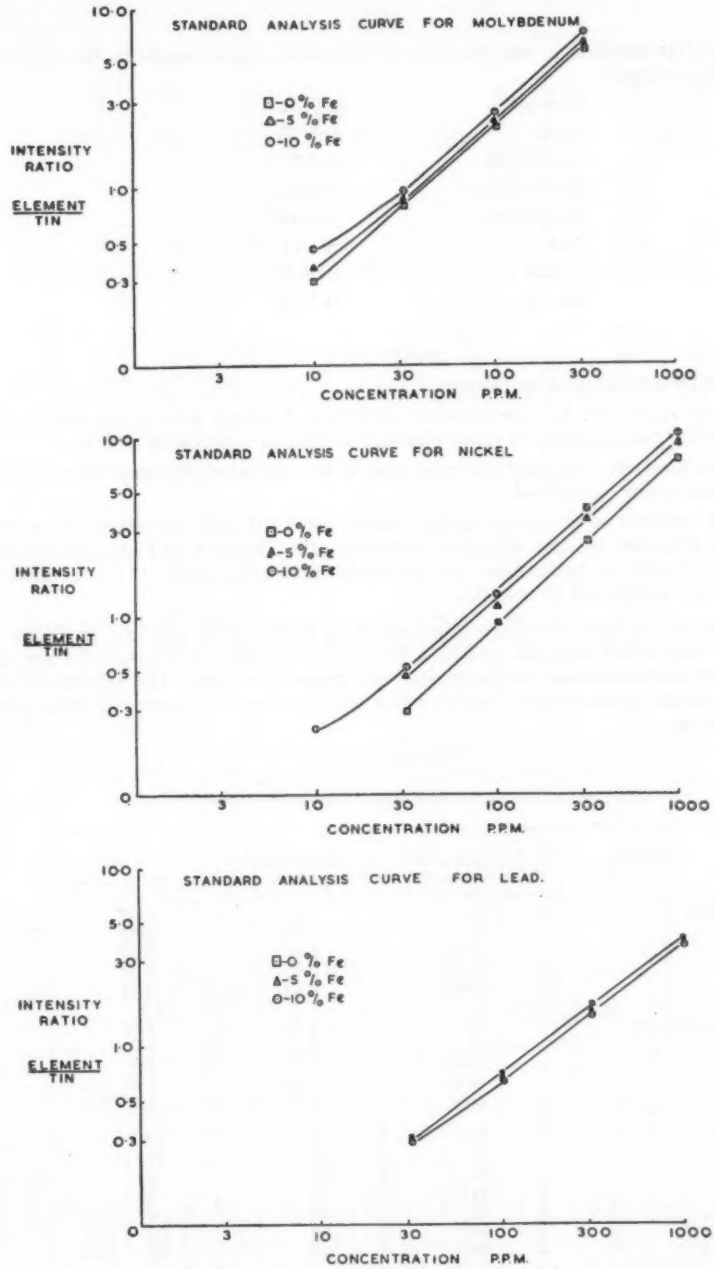

Fig. 1—Influence of iron concentration on the standard analysis curves

Using 10 g samples, it was possible to determine the elements in the following concentration ranges:

Element	*p.p.m.*
Lead	0·3-10
Vanadium	0·3-3
Molybdenum	0·05-3
Manganese	3·0-150
Zinc	5-100
Cobalt	0·05-20
Nickel	0·2-10

RESULTS

The method was tested as follows:

(i) A recovery test for the elements zinc, molybdenum and cobalt was carried out by varying the amounts of these elements added to samples of lucerne.

(ii) The analysis of a plant material sample was repeated eighteen times and the standard deviation calculated.

(iii) A number of standard samples were analysed and the results compared with those obtained by the Macaulay Institute, the Division of Chemical Services of the Department of Agriculture and previous results obtained by the Council for Scientific and Industrial Research[7].

The results of these tests are summarised in Tables I, II and III. In Table III results for two other samples analysed by various American laboratories are also given. These were analysed for only zinc, manganese and iron. The results for iron were determined approximately as this value was only used to locate the appropriate working curve.

TABLE I

Results of recovery tests for the elements zinc, molybdenum and cobalt

Element	Amount added in p.p.m. (a)	Concentration in p.p.m. (b)	b-a p.p.m.
Cobalt	0	0·32	0·32
	0	0·33	0·33
	0·10	0·47	0·37
	0·20	0·52	0·32
	0·50	0·94	0·44
Molybdenum	0	1·35	1·35
	0	1·3	1·3
	0·20	1·7	1·5
	0·40	1·95	1·55
	0·60	2·2	1·6
Zinc	0	10	10
	0	12	12
	10	19	9
	20	27	7
	20	29	9
	40	52	12
	60	73	13

TABLE III

Comparison of analytical results (all values given in p.p.m.)

Sample		Pb	Mo	V	Co	Ni	Mn	Zn	Fe
4A	1*	1·4	0·10	0·23	0·08	2·4	58	10	150
Peach	2**	1·7	0·07	0·22	0·17	2·6	49	24	182
leaves	3***	—	(0·04-0·1)	(0·20-0·30)	(0·1-0·3)	(2·2-3·3)	(42-58)	(21-28)	(165-190)
4B	1	3·9	2·5	0·56	0·28	5·0	37	54	360
Bean	2	3·0	2·0	0·7	0·23	5·6	43	59	328
leaves	3	(2·2-3·9)	(1·7-2·3)	(0·51-1·0)	(0·1-0·4)	(4·7-6·6)	(32-53)	(54-60)	(300-340)
4C	1	1·3	1·1	0·4	0·31	2·4	168	19	280
Beet	2	1·35	0·95	0·5	0·20	2·5	161	23	260
leaves	3	(1·3-6·0)	(0·7-1·4)	(0·4-0·7)	(0·1-0·4)	(2·0-3·3)	(139-182)	(18-30)	(255-263)
4D	1	2·0	5·3	0·7	0·25	3·1	84	48	
Gem	2	—	4·5	1·0	0·32	3·4	91	49	
leaves	3	(2·7-5·5)	(3·3-5·5)	(0·9-1·1)	(0·15-0·5)	(3·0-4·0)	(77-109)	(38-60)	
4E	1	3·0	0·03	0·2	0·61	1·33	145	35	145
Plum tree	2	—	0·05	0·23	0·6	1·7	136	62	154
leaves	3	(0·5-5·5)	—	(0·13-0·3)	(0·5-0·8)	(1·3-2·1)	(125-150)	(30-90)	(150-160)
4H	1	1·2	0·1	0·47	0·91	9·7	75	21	270
Tobacco	2	—	0·1	0·35	0·93	9·8	67	35	260
	3	(0·2-2·0)	(0·04-0·2)	(0·25-0·5)	(0·8-1·2)	(7·0-12·5)	(62-69)	(28-50)	—
4I	1	1·8	0·13	2·0	2·03	12·3	76	42	790
Tobacco	2	1·4	0·18	2·5	2·2	13·5	70	51	1040
	3	(0·8-2·0)	(0·05-0·3)	(1·5-4·0)	(1·7-2·9)	(11·6-17·0)	(68-72)	(45-60)	(920-1200)
4J	1	—	0·32	0·98	0·7	3·8	150	80	
Rumen	2	60	0·29	1·45	0·5	2·0	145	71	
	3	—	(0·1-0·45)	(1·4-1·5)	(0·2-1·0)	(1·6-2·5)	(67-180)	(53-105)	
3	1	Not analysed for these elements as figures not available for comparison.					26	75	500
Citrus	2						33	77	455
leaves	3						(23-46)	(62-90)	(275-560)
4	1	Not analysed for these elements as figures not available for comparison.					66	26	280
Peach	2						80	32	230
leaves	3						(61-94)	(23-39)	(140-277)

*1. Results obtained (average of 1 to 3 samples).
**2. Average value of various other methods used to analyse samples (Strasheim and Camerer[7])
***3. Range of results of other methods

TABLE II

The reproducibility of the analysis results for the elements lead, vanadium, molybdenum, manganese, zinc, cobalt and nickel

Element	Average amount in p.p.m.	Standard Deviation in p.p.m.	Coefficient of variation
Lead	2·0	0·15	7·5
Vanadium	0·23	0·04	17·4
Molybdenum	1·0	0·18	18·0
Manganese	25·5	3·2	12·5
Zinc	29·0	4·0	13·8
Cobalt	0·38	0·03	7·9
Nickel	3·3	0·4	12·1

CONCLUSION

From the results given in Tables I, II and III the following may be concluded:

(1) The results of the recovery tests for the elements cobalt, molybdenum and zinc are fair when the concentration levels of the elements are considered. It appears that there is no necessity for as much as 40 mg of iron to be present for satisfactory recovery of the trace elements[8]. (In the case of the material used for the recovery tests there was no more than 5 mg of iron present in the sample).

(2) The reproducibility tests seem to indicate that the precision of the method is not as high as that attained by Scharrer and Judel[3]. This may be due to their use of iron instead of tin as internal standard for all elements except zinc. For zinc they used cadmium. However, they give no precise indication of the actual element concentrations in the sample used for their reproducibility test.

(3) Some of the zinc results obtained were low. This was possibly due to inadequate temperature control during the ashing of the samples and the charring of the organic extract. (Test samples ashed at higher temperatures gave low zinc results). Subsequently it was found that with careful temperature control better results were obtained.

(4) The concentration procedure used with this method is relatively simple and fast. No chemical determination of the iron content is necessary. The method, in comparison with the one developed by Mitchel and co-workers, has the added advantage that it is possible to determine the manganese satisfactorily with the other elements[8]. The method should be suitable for diagnostic work in plant and animal trace element physiological studies, the reproducibility of the results being sufficient for this purpose.

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THE ACCURATE DETERMINATION OF BORON IN PLANT MATERIAL

by

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OPSOMMING

Die belangrikste faktore wat die bepaling van boor in plante, volgens die kurkumin-metode, beïnvloed, is ondersoek. 'n Gewysigde metode wat akkurate en presiese resultate lewer, word beskryf. Daar is gevind dat gewone glasapparaat geskik is, dat alleen 'n lae konsentrasie van sure gebruik word en dat die elemente wat normaalweg in plante aanwesig is geen nadelige invloed op die bepaling het nie.

SUMMARY

A critical investigation of the curcumin method for the determination of boron in plant materials is presented. A modified method, which is both accurate and precise, is described. Ordinary laboratory glassware was found to be suitable, only acids of low concentrations are used, and none of the elements normally occurring in plant material interfere in the determination.

Curcumin reacts with boric acid in an alcoholic medium to give rubrocurcumin, and when an acidified solution of this isomer is avaporated to dryness, the red complex, rosocyanin is formed. Rosocyanin is soluble in alcohol and is formed in amounts proportional to the amount of boric acid present. The colour change taking place is from yellow to red.

Several methods for the determination of small amounts of boron using curcumin have been described in the literature[1, 2, 3].

The work described here was undertaken in order to investigate these methods with a view to modifying them for the accurate routine determination of boron in plant material.

EXPERIMENTAL

Apparatus and reagents. All colorimetric measurements were carried out on a Cenco Sheard Spectrophotelometer (Cat. No. 29450) using 1 cm glass cells. Well leached soda or pyrex glassware was found to be quite satisfactory for the temporary measurement of volumes. Ashing of plant material and evaporation of solutions were carried out in porcelain ware without any influence on the boron content. Pure water was obtained by passing distilled water through an ion-exchange column containing a "mixed-bed" resin (Amberlite MB_3). All standard solutions and solutions containing foreign ions (for interference tests) were prepared from Johnson Matthey "Specpure" chemicals. All other solid reagents were of "Analar" grade.

Transmittance curves. Dible *et al.*[3] recorded the spectral separation of the two colour components in an ethyl alcohol medium, but unfortunately they did not present the effects of the one component in the presence of the other, or in the presence of oxalic acid. These effects are graphically represented in Figs. 1A and 1B. From the transmittance curves of rosocyanin and curcumin in the presence of 5% oxalic acid it is seen that maximum spectral separation was attained at 555mμ at both high (10μg of B) and low (1μg of B) concentrations of boron.

The influence of pH on the development of colour. Dible, Truog and Berger[3], do not adjust the pH prior to the development of the colour. Silverman and Trego[4], using acetone as a developing solvent throughout, effect a pH adjustment using sodium carbonate and hydrochloric acid. This procedure involves the addition of sodium carbonate (0·1 g) to the test aliquot followed by an evaporation to dryness at 110°C. The pH is then adjusted by first neutralising with hydrochloric acid (1:4) using phenolphthalein, and then adding 0·5 ml in excess.

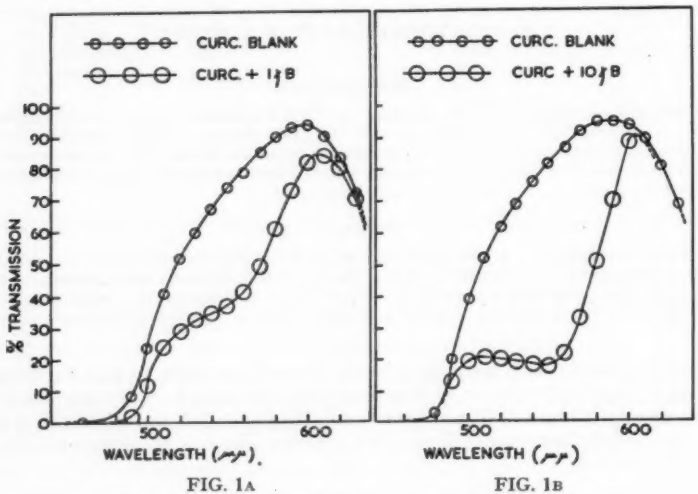

FIG. 1A FIG. 1B

The transmission curves of curcumin and rosocyanin

During the course of this study, such an adjustment of pH was found essential. The addition of 0·06±0·01 g of sodium carbonate per sample, when evaporating a 4-8 ml test aliquot to dryness, was found to be sufficient in order to eliminate any loss of boron by volatilisation.

The effect of excess acid on the colour development was next investigated. Maximum colour development was attained by using an excess of 1·2 ml of hydrochloric acid (1:8) per sample.

The presence of oxalic acid indicated a possible buffering action on the pH, and a resultant stabilising effect on the colour reaction. The use of larger concentrations of oxalic acid was investigated and maximum buffering action was obtained with 0·4 g per sample (using a 10% oxalic-0·04% curcumin reagent). The use of this higher concentration of oxalic acid also had a stabilising effect on the keeping quality of the curcumin reagent.

The influence of temperature on the development of colour. Naftel,[2] Hafford,[5] and Russell,[6] were among the first workers to claim the necessity of developing the colour by evaporating at 55± 3°C. Using a modified procedure, determinations were carried out at different evaporation temperatures. The results are recorded in Fig. 2. It is clear that maximum colour development occurred when the reaction products were dried at 53°C, and that evaporations carried out at 55± 3°C would introduce an error of 4-6% at concentrations of 2·0-3·5 µg B per test sample. Perfectly reproducible results free of any such error were obtained within the limits 53±2°C.

The influence of the drying period on the development of colour. In the method of Dible, Berger and Truog[3] the concentration of the hydrochloric acid varied, since no initial adjustment of pH was made. On evaporating a test sample at 55°C and baking for a further specified 15 minutes, the evaporation of the hydrochloric acid is in no way controlled. Since it was found that the final pH of the dried reaction products influenced the amount of colour development, as well as the stability of the final colour solutions, different drying techniques were investigated.

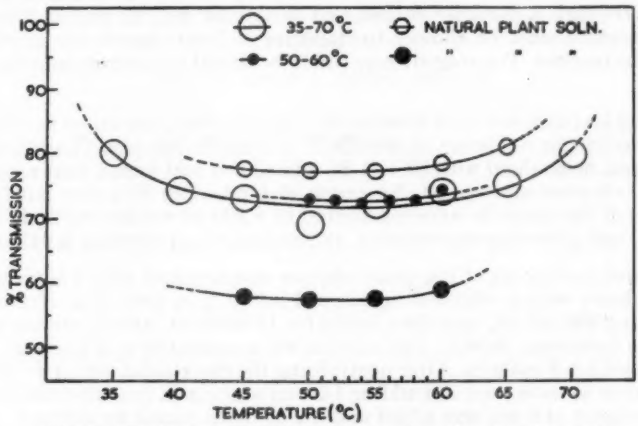

FIG. 2—The influence of temperature on the colour development

Different methods of controlling the rate of evaporation of the hydrochloric acid were tested with the object of observing the effect on the colour development. It was found that the specified 15 minute drying time was not sufficient, tending to give non-reproducible results. When the colour was developed in deep 250 ml porcelain fusion crucibles it took 3 hours drying time before stable conditions were reached, whilst using open evaporating dishes and a forced draught, 30 minutes sufficed. When carried out on normal plant solutions using open dishes and no forced draught, it was found that stable development was reached after 45 minutes of baking at 53°C. The final colour solutions resulting from a short drying period (therefore high in hydrochloric acid content) were not optically stable on standing, the stability increasing with length of drying period and increase in oxalic acid content.

The dry ashing of plant material. McHargue and Hodgkiss,[7] Hafford,[5] and Berger and Truog,[8] have shown that plant material does not lose boron when ashed at 550°. These authors explain this phenomenon as being due to the high content of natural bases in the plant material preventing any volatilisation of boron from taking place. Experiments carried out on 1·000 g samples taken from a large composite sample of dried citrus leaf material indicated that no boron was lost when ashing for up to 12 hours at temperatures up to 800°C. However, samples that had been moistened before ashing readily lost boron, indicating the critical nature of the organo-boric acid complexes in preventing boron volatilisation. Accordingly, leaf samples were ashed at 500-550°C for 6-8 hours in completely dry porcelain casserole dishes, followed by a mild acid extraction.

Determination of boron in leaf materials. All solutions and pure water were stored in polythene bottles to avoid ion-exchange between the solution and the walls of the container.

The stock boron standard was prepared by dissolving 1·4289 g H_3BO_3 in 100 ml water. When preparing calibration curves, this solution was diluted to contain 0·5 μg B per ml.

A mixed curcumin-oxalic acid reagent was prepared by dissolving finely ground curcumin (0·50 g) and oxalic acid crystals (50·0 g) in 95% ethyl alcohol (500 ml) in a polythene container. The mixture was placed in a waterbath at 50-60°C for 1 hour, shaking at intervals to assist solution. The solution was then cooled to about −5°C and filtered through a Buchner funnel and Whatman No. 42 paper. Prepared as above, the mixture must be allowed to stand for 48 hours before use in order that equilibrium be reached. The reagent may safely be stored in a refrigerator for at least five weeks.

Powdered leaf material (1 g) dried at 65°C for 24 hours, was ashed in a small, dry porcelain casserole for 6-8 hours at 500-550°C in a muffle furnace. The ashed residue was cooled and neutralised with HCl (1:8), adding the acid from a dispensing microburette until effervescence ceased. An excess of 1 ml. (1:8) HCl was finally added. The contents of the casserole were transferred to a 200 ml volumetric flask, made up to the mark, and after thorough mixing, transferred to a polythene bottle.

An aliquot (1-5 μg B) of the clear solution was buretted into a 9 cm porcelain evaporating basin with a siliconed lip (dipped into a $\frac{1}{4}$ in. pool of a solution of 1% Dowex Corning 200 in CCl_4 and then baked for 12 hours at 200°C), containing anhydrous sodium carbonate (0·06 g). The solution was evaporated to dryness on a waterbath and cooled for 5 minutes. After neutralising the dry residue with 1:8 HCl (using phenolphthalein as indicator) and adding 1·20 ml of the acid in excess, the curcumin-oxalic acid reagent (4·0 ml) was added and the contents mixed by swirling. The mixture was then evaporated to dryness on a waterbath controlled at 53±2°C. After complete dryness, the residue was baked for 45 minutes at the same temperature. The cooled residue (10 mins) was dissolved in a small volume of 95% ethyl alcohol, filtered through Whatman No. 40 into a 100 ml volumetric flask, washed with 95% ethyl alcohol, and finally made up to the mark with alcohol. The transmittance of the solution was determined at 555 mμ. Measurements should be carried out not later than 3 hours after making up with alcohol. A calibration curve was prepared by treating standard solutions containing different concentrations of boron (0-6 μg) exactly as above.

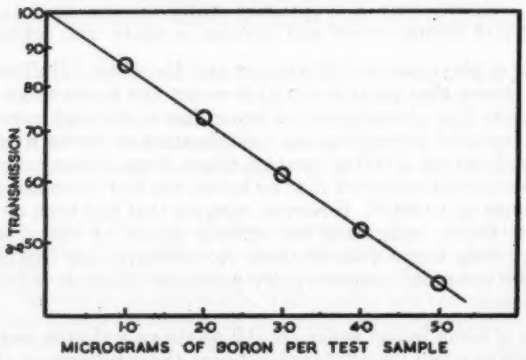

FIG. 3—Standard reference curve for the determination of boron

Used alcohol may be recovered by distilling in the presence of calcium hydroxide.

RESULTS

In Tables I and II, experimental results showing the reproducibility and accuracy of the method are tabulated. Fig. 3 represents a working curve of transmission vs. concentration of B.

TABLE I

Recovery tests from synthetic standards

No.	Foreign ions added (μg)								Boron (μg)	
	P	Ca	Mg	K	S	Fe	Mn	Zn	Theoretical	Found
1	1·2	6·2	5·0	1·5	7·2	0·2	0·8[5]	0·2[5]	2·00°	1·98[6]
2	2·5	12·5	10·0	3·0	14·4	0·5	1·7	0·5	2·00°	2·00[8]
3	3·7	18·7	25·0	4·5	21·6	0·7	2·6[5]	0·7[5]	2·00°	1·98[6]
4	5·0	25·0	20·0	6·0	28·8	1·0	3·5	1·0	2·00°	1·98[6]
5	6·2	31·2	25·0	7·5	36·0	1·2	4·3[5]	1·2[5]	2·00°	2·00°
6	7·5	27·5	30·0	9·0	43·2	1·5	5·2[5]	1·5	2·00°	1·98[6]
7	8·7	43·7	35·0	10·5	50·4	1·7	6·0	1·7[5]	2·00°	1·98[1]
8	10·0	50·0	40·0	12·0	57·6	2·0	7·0	2·0	2·00°	1·98[6]

TABLE II

Recovery tests from plant solutions

No.	% Transmission. 1·000° g samples	Mean B content (μg)	% Transmission. 0·500° g samples + 1·00 μg B	Mean B content (μg)	Mean % recovery
1	70·6		71·4		
2	70·3		70·4		
3	70·7	2·00	71·0	1·96	98
4	70·3		71·0		
5			71·3		

The precision of the method was tested by carrying out 20 separate determinations on a well-mixed citrus leaf sample. With a mean boron content of 109 p.p.m. a standard deviation of 2·1 p.p.m. was obtained, i.e., a percentage standard deviation of 1·9.

DISCUSSION

From these results it is clear that the modified method is both precise as well as accurate. It eliminates the use of concentrated acids, a serious defect of some of the other methods for determining boron. The method is reasonably rapid and especially adaptable to routine analysis—a batch of 12 determinations can conveniently be carried out in 4-5 hours. The method is very economical as regards the use of reagents, and it is carried out using ordinary laboratory apparatus. Many of the alternative methods involve the use of boron-free glassware. The method has been tested on a large number of citrus and pineapple leaf samples from different areas, varying in boron content from 6 to over 200 p.p.m. In all cases, the results have been entirely satisfactory.

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DIE FOTOLITIESE ONTBINDING VAN KETONE BY HOË TEMPERATURE. DEEL I. ASETOON

deur

J. A. VAN DEN BERG en V. PRETORIUS

SUMMARY

The photolysis of acetone at elevated temperatures has been studied using a mass spectrometer. A series of elementary reactions to account for the observed reaction products and kinetics has been put forward. In particular the mechanism of the formation of ethylene during the decomposition has been investigated.

OPSOMMING

Die fotolise van asetoon by hoë temperature is met behulp van 'n massaspektrometer ondersoek. 'n Reeks elementêre reaksies word voorgestel om 'n verklaring te gee van die waargenome produkte en kinetika. In besonder is die meganisme van die vorming van etileen gedurende die ontbinding nagegaan.

INLEIDING

Die meganisme van die fotolitiese ontbinding van asetoon by hoë temperature is reeds breedvoerig ondersoek[1, 2, 3, 4, 5]. Die vernaamste reaksieprodukte, wat 'n verklaring bied vir sowat 95% van die totale ontbinding[3], is kwantitatief vasgestel as metaan, etaan, koolstofmonoksied en metieletielketoon. Melding word gemaak van klein, maar in die meeste gevalle onbepaalde, hoeveelhede van propaan[3], keteen[4, 7], asetonielasetoon (biasetoniel),[4] en diasetoon[4].

Dit word algemeen aanvaar dat die kinetika en vernaamste reaksieprodukte verklaar word deur die volgende elementêre reaksies:

$$CH_3COCH_3 + lig = 2\,\dot{C}H_3 + CO \quad .. \quad .. \quad .. \quad .. \quad (1)$$

$$2\,\dot{C}H_3 = C_2H_6 \quad .. \quad .. \quad .. \quad .. \quad (2)$$

$$\dot{C}H_3 + CH_3COCH_3 = CH_4 + \dot{C}H_2COCH_3 \quad .. \quad .. \quad .. \quad .. \quad (3)$$

$$\dot{C}H_3 + \dot{C}H_2COCH_3 = C_2H_5COCH_3 \quad .. \quad .. \quad .. \quad .. \quad (4)$$

$$2\,\dot{C}H_2COCH_3 = (CH_2COCH_3)_2 \quad .. \quad .. \quad .. \quad .. \quad (5)$$

Vir die ontstaan van etileen bestaan daar nog geen bevredigende verklaring nie. Mandelcorn en Steacie[5] stel voor dat die etileen gevorm word deur die ontbinding van die $CH_3COCH_2\dot{C}H_2$-radikaal, wat op sy beurt gevorm word deur die reaksie van metielradikale met die gevormde metieletielketoon:

$$\dot{C}H_3 + CH_3COC_2H_5 = CH_4 + CH_3COCH_2\dot{C}H_2 \quad .. \quad .. \quad .. \quad (6)$$

$$CH_3COCH_2\dot{C}H_2 = \dot{C}H_3 + CO + C_2H_4 \quad .. \quad .. \quad .. \quad (7)$$

Long[8], daarenteen, is van mening dat die etileen as volg ontstaan:

$$\dot{C}H_3 + C_2H_6 = CH_4 + \dot{C}_2H_5 \quad .. \quad .. \quad .. \quad .. \quad (8)$$

$$\dot{C}H_3 + \dot{C}_2H_5 = C_3H_8 \quad .. \quad .. \quad .. \quad .. \quad (9)$$

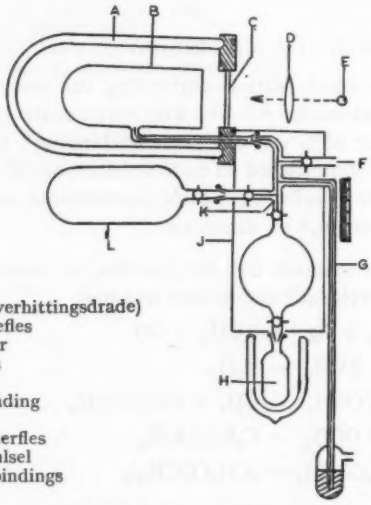
$$\dot{C}H_3 + C_3H_8 = CH_4 + \dot{C}_3H_7 \quad .. \quad .. \quad .. \quad .. \quad (10)$$

$$\dot{C}_3H_7 = \dot{C}H_3 + C_2H_4 \quad .. \quad .. \quad .. \quad .. \quad (11)$$

Die reaksies (6) . . . (12) is tot nog toe nie deur eksperimentele gegewens gestaaf nie. In die onderstaande ondersoek is 'n massaspektrometer gebruik om eksperimentele data te verkry waaruit 'n gevolgtrekking gemaak kan word i.v.m. die vormingswyse van etileen gedurende die fotolise.

EKSPERIMENTELE BESONDERHEDE EN RESULTATE

'n Skematiese diagram van die apparaat wat in hierdie ondersoek gebruik is, word in Fig. 1 aangetoon. 'n Silindriese, kwarts reaksiefles (9 cm lank en 2·5 cm deursnee), wat met optiese plat vensters voorsien is, is in 'n spesiale oond[9] gemonteer. Die temperatuur van die oond kon binne 0·2° C oor die gebied 240-310° beheer word. Die ligbron het bestaan uit die volle straling van 'n hoë druk kwiklamp (Zeiss VZ Dr Hg 200). Die inlaatsisteem, wat aan die reaksiefles grens, is binne 'n geïsoleerde omhulsel by 60°C gehou sodat die kondensasie van die reaksieprodukte verhinder is.



A Oond (sonder verhittingsdrade)
B Kwarts reaksiefles
C Kwarts venster
D Kollimatorlens
E Kwiklamp
F Vakuumverbinding
G Manometer
H Asetoon monsterfles
J Verhitte omhulsel
K Kapillêre verbindings
L Analise-fles

FIG. 1—Fotolise-apparaat

Analitiese graad asetoon, wat verder gesuiwer is deur fraksionele distillasie in 'n kolom met 20 teoretiese plate, is vir al die eksperimente gebruik. Die asetoon is oor anhidriese natriumsulfaat in 'n donker fles bewaar. Die monsters van die asetoon is telkens in die fotolise-apparaat vervang. Die opgeloste lug in die asetoon is verwyder deur die monster herhaaldelik te vries en uit te pomp.

Monsters van die gasmengsel in die reaksiefles is aan die einde van elke bestraling, sonder verdere behandeling, verwyder vir massaspektrometriese analise.

Drie reekse eksperimente is uitgevoer. Eerstens is 'n konstante hoeveelheid asetoon, manometries gemeet, bestraal vir 'n konstante tydsduur, by een van 'n reeks vaste temperature in die gebied 240-310°C. Die tydsduur is sodanig gekies dat die ontbinding tot ongeveer 10% beperk is, om sodoende newereaksies uit te skakel. In die tweede reeks is die reaksietemperatuur konstant gehou en verskillende hoeveelhede asetoon 'n konstante tyd lank bestraal. Vir die derde reeks is die reaksietye verander terwyl die temperatuur en die hoeveelheid asetoon konstant gehou is. Die massaspektrometriese analises van die gasmengsels word in Tabelle I, II en III aangegee.

TABEL I

Die fotolise van asetoon by verskillende temperature

Aanvangsdruk: 100 mm Hg
Bestralingsduur: 300 sekondes

Eks. nr.	Temp. T, °K	[A]	R_{CO}	R_M	R_E	R_{Mek}	R_{Bias}	R_{En}
1	580	1·66	8·8	7·3	3·00	3·00	2·16	0·31
2	565	1·71	8·6	6·3	3·43	3·03	1·63	0·26
3	549	1·76	8·6	5·3	3·76	2·94	1·18	0·23
4	536	1·80	8·4	4·7	4·1	2·70	1·00	0·19
5	522	1·85	7·8	3·7	4·5	2·23	0·74	0·13

[A] : konsentrasie asetoon in molekules $cm^{-3} \times 10^{-18}$
R : vormingsnelheid in molekules $cm^{-3}sek^{-1} \times 10^{-18}$
Eks. nr. : eksperimentnommer
°K : temperatuur, T, in grade Kelvin
M : CH_4
E : C_2H_6
Mek : $C_2H_5COCH_3$
Bias : $(CH_3COCH_3)_2$
En : C_2H_4

TABEL II

Die fotolise van asetoon by verskillende aanvangsdrukke

Temperatuur: 274°C
Bestralingsduur: 240 sekondes

Eks. nr.	[A]	R_{CO}	R_M	R_E	R_{Mek}	R_{Bias}	R_{En}
6	0·353	1·46	0·48	0·86	0·33	0·08	—
7	0·880	4·0	2·04	2·07	1·35	0·35	0·07
8	1·76	8·0	5·07	3·90	2·87	1·20	0·18
9	2·21	10·4	6·9	4·27	3·60	1·65	0·29
10	2·64	12·4	8·4	5·6	4·4	2·0	0·32
11	3·53	15·5	11·5	5·15	4·7	3·4	0·35

TABEL III

Die fotolise van asetoon vir verskillende bestralingstye

Temperatuur: 274° C
Aanvangsdruk: 100 mm Hg

Eks. nr.	Tyd. Sek.	[A]	R_{CO}	R_M	R_E	R_{Mek}	R_{Bias}	R_{Et}
12	22	1·765	8·4	3·7	3·1	4·45	—	*
13	44	1·765	8·2	5·6	4·7	4·0	0·80	*
14	81	1·765	8·9	5·0	3·8	3·1	0·98	*
15	144	1·765	8·0	4·7	3·9	3·3	0·67	0·09
16	254	1·765	8·3	5·0	4·0	2·5	1·25	0·15
17	323	1·765	8·5	5·1	3·7	2·3	1·39	0·17

* etileen te gering om te bepaal

Die noukeurigheid van die hoeveelhede koolstofmonoksied, metaan, etaan en metieletielketoon is ongeveer 10%. Die bepaling van die etileen is heelwat minder akkuraat aangesien die berekening berus op die klein verskille tussen betreklik groot hoeveelhede.

Biasetoniel is nie direk bepaal nie omdat dit in die monsterhouer kondenseer en geneig is om in die kraanvet op te los. In plaas daarvan om spesiale tegnieke[10] te ontwikkel om hierdie produk te bepaal, is dit indirek bereken uit die vergelyking:

$$R_{(CH_3COCH_2)_2} = \tfrac{1}{2}(R_{CH_4} - R_{CH_3COC_2H_5})$$

wat uit die reaksiereeks (1), (2), . . . (5) volg.

Geen propaan kon waargeneem word nie.

BESPREKING

Die aanvaarde reaksiereeks (1), . . . (5) maak nie voorsiening vir die vorming van die klein hoeveelhede etileen nie. Dit is onwaarskynlik dat etileen volgens reaksies (6) en (7), of volgens die reeks (8), . . . (11) sou gevorm word, vanweë die lae konsentrasies van metieletielketoon en van etaan in die beginstadium van die ontbinding, en vanweë die betreklike hoë aktiveringsenergië van die betrokke reaksies. Teen die reaksies (8), . . . (11) moet verder aangemerk word dat C_2H_4 ten koste van CH_4 en C_2H_6 gevorm sou word, in stryd met die eksperimentele bevindinge, soos later sal blyk. Ons is van mening dat 'n tipe van disproporsionasie van die asetonielradikale waarskynliker is, nl:

$$2\,CH_3COCH_2 = 2\,CH_3 + 2\,CO + C_2H_4 \quad .. \quad .. \quad .. \quad .. \quad (12)$$

Hierdie bewering kan getoets word deur die teorie van stasionêre toestande op die reaksiereeks (1), . . . (5), (12) toe te pas, en die afleidings daaruit met die eksperimentele bevindinge te vergelyk.

Indien $k_1, k_2, \ldots k_6$ die onderskeie snelheidskonstantes van die reaksies (1), . . . (5), (12) voorstel, kan die snelheidsvergelykinge soos volg weergegee word:

$$R_{CO} = k_1 I_a \quad I_a = \text{die ligintensiteit}^1.$$
$$R_{C_2H_6} = k_2[\dot{C}H_3]^2$$
$$R_{CH_4} = k_3[\dot{C}H_3][CH_3COCH_3]$$
$$R_{C_2H_5COCH_3} = k_4[\dot{C}H_3][\dot{C}H_2COCH_3]$$
$$R_{(CH_3COCH_2)_2} = k_5[CH_3CO\dot{C}H_2]^2$$
$$R_{C_2H_4} = k_6[CH_3CO\dot{C}H_2]^2$$

Hieruit volg nou:

$$R_{CH_4} / R^{\frac{1}{2}}_{C_2H_6} \times [CH_3COCH_3] = k_3 / k_2^{\frac{1}{2}} \quad \text{(a)}$$
$$R^{\frac{1}{2}}_{C_2H_6} \times R^{\frac{1}{2}}_{(CH_3COCH_2)_2} / R_{CH_3COC_2H_5} = k_2^{\frac{1}{2}} \times k_5^{\frac{1}{2}} / k_4 \quad \text{(b)}$$
$$R^2_{CH_3COC_2H_5} / R_{C_2H_6} \times R_{C_2H_4} = k_4^2 / k_2 \times k_6 \quad \text{(c)}$$
$$R_{C_2H_4} / R_{(CH_3COCH_2)_2} = k_6 / k_5 \quad \text{(d)}$$

Die eksperimentele data van Tabelle I, II en III kan gebruik word om die geldigheid van die vergelykings (a), (b), (c) en (d) te toets, soos aangedui in Tabelle IV en V.

TABEL IV

Die eksperimentele waardes vir die verhoudings (a), (b), (c) en (d) by verskillende temperature, 240-310°C

Eks. nr.	°K	$\frac{R_M}{R^{\frac{1}{2}}_E \times [A]}$	$\frac{R^{\frac{1}{2}}_E \times R^{\frac{1}{2}}_{Bias}}{R_{Mek}}$	$\frac{R^2_{Mek}}{R_E \times R_{En}}$	$\frac{R_{En}}{R_{Bias}}$
1	580	256·2	0·84	9·7	0·14
2	565	198·8	0·78	10·2	0·16
3	549	154·8	0·71	10·0	0·20
4	536	128·8	0·74	9·4	0·19
5	522	95·1	0·82	8·6	0·17

Tabelle IV en V toon aan dat die verhoudings (c) en (d), binne die eksperimentele fout, konstant bly. Dit bewys die geldigheid van etileenvorming volgens reaksie (12), in teenstelling met die alternatiewe reaksies (6) en (7), of (8) . . . (11), wat nie die vergelykings (c) en (d) lewer nie.

Omdat reaksies (2), (4), (5) en (12) almal vry radikaal-herkombinasies is, is hulle aktiveringsenergië baie klein. Om hierdie rede sal die verhoudings (b), (c) en (d) nie met temperatuur verander nie. Hierdie gevolgtrekking word gestaaf deur die eksperimentele resultate in Tabel IV.

TABEL V

Die eksperimentele waardes vir die verhoudings (a), (b), (c) en (d) by 'n konstante temperatuur, 274°C

Eks. nr.	$\frac{R_M}{R_E^{\frac{1}{2}} \times [A]}$	$\frac{R_E^{\frac{1}{2}} \times R_{Bias}^{\frac{1}{2}}}{R_{Mek}}$	$\frac{R_{Mek}^2}{R_E \times R_{En}}$	$\frac{R_{En}}{R_{Bias}}$
6	146	0·79	—	—
7	167	0·63	12·4	0·20
8	147	0·76	11·8	0·15
9	151	0·74	10·5	0·18
10	148	0·71	12·1	0·16
11	140	0·89	11·2	0·10
13	135	0·48	—	—
14	145	0·64	—	—
15	134	0·49	—	0·13
16	143	0·89	10·8	0·12
17	151	0·97	8·5	0·12

Die verandering van verhouding (a) met temperatuur (Table IV) is gebruik om die verskil in aktiveringsenergie $E_3 - \frac{1}{2}E_2$ te bereken soos aangetoon is in Fig. 2. Uit die helling van hierdie kromme volg dat $E_3 - \frac{1}{2}E_2 = 9{\cdot}6$ kkal/mol$\div E_3$ (omdat $E_2 \div 0$) wat goed ooreenstem met die resultate van ander werkers[1, 4, 5].

Die lineariteit van die kromme in Fig. 2 steun die geldigheid van reaksies (1)—(5), (12).

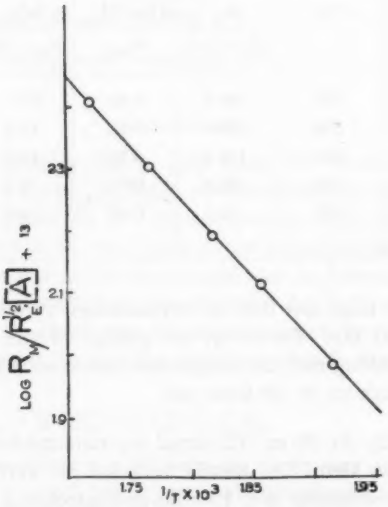


FIG. 2—Verandering van log $R_M/R_E^{\frac{1}{2}}[A]$ met I/T

Ten slotte volg dit uit reaksies (1)—(5), (12) dat

$$R_{CO} = R_E + \tfrac{1}{2}R_M + \tfrac{1}{2}R_{Mek}$$

d.w.s. die materie-balans

$$m = (R_E + \tfrac{1}{2}R_M + \tfrac{1}{2}R_{Mek}) \; / R_{CO} \doteqdot 1.$$

Die geringe hoeveelheid etileen word buite rekening gelaat.

Die eksperimenteelbepaale waardes van m word in Tabel VI aangegee en vergelyk goed met die teoretiese waarde.

TABEL VI

Eksperimentele waardes vir die massa-balans m

Eks. nr.	1	2	3	4	5	6	7	8	9	10	11	12
m	0·92	0·94	0·92	0·93	0·95	0·87	0·93	0·98	0·92	0·92	0·89	0·87

Dank word uitgespreek teenoor die Wetenskaplike Nywerheidsnavorsingsraad vir die gebruik van 'n massaspektrometer en die toekenning van 'n beurs aan een van die skrywers (J.A.v.d.B); teenoor African Explosives and Chemical Industries Ltd. vir die toekenning van 'n "Research Fellowship" aan die ander skrywer (V.P.).

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DIE FOTOLITIESE ONTBINDING VAN KETONE BY HOË TEMPERATURE. DEEL II. METIELETIELKETOON

deur

J. A. VAN DEN BERG en V. PRETORIUS

SUMMARY

A mass spectrometer has been used to study the products formed during the photolysis of methyl ethyl ketone at elevated temperatures (200°-300°C). A reaction scheme to account for the observed products and kinetics of the decomposition has been put forward.

OPSOMMING

'n Massaspektrometer is aangewend vir die ontleding van die produkte wat gedurende die fotolise van metieletielketoon by hoë temperature (200°-300° C) ontstaan. 'n Reaksieskema, wat 'n verklaring bied vir die waargenome produkte en die kinetika van die ontbinding, word voorgestel.

INLEIDING

In teenstelling met die fotolise van asetoon, wat breedvoerig ondersoek is, het die meganisme van die fotolise van metieletielketoon betreklik min aandag geniet. Die twee reaksies kom in vele opsigte ooreen, veral in die sin dat vry radikale in albei gevalle 'n oorwegende rol speel. Dit is egter duidelik dat die fotolise van metieletielketoon moeiliker interpreteer kan word weens die groter verskeidenheid van produkte[1, 2, 3].

Koolstofmonoksied, metaan, etaan, propaan, butaan en etileen is kwantitatief vasgestel in die produkte by hoë temperature[1, 2, 3]. By laer temperature word asetoon, di-etielketoon, bipropioniel[3] en biasetiel[4] ook waargeneem.

Volgens Ausloos en Steacie[5] vind die volgende reaksies plaas gedurende die fotolise van metieletielketoon tussen 200° en 300°C:

$$CH_3COC_2H_5 + \text{lig} = \dot{C}H_3 + \dot{C}_2H_5 + CO \quad .. \quad .. \quad (1)$$

$$\dot{C}H_3 + CH_3COC_2H_5 = CH_4 + CH_3CO\dot{C}_2H_4 \quad .. \quad .. \quad (2)$$

$$\dot{C}_2H_5 + CH_3COC_2H_5 = C_2H_6 + CH_3CO\dot{C}_2H_4 \quad .. \quad .. \quad (3)$$

$$\dot{C}H_3 + \dot{C}H_3 = C_2H_6 \quad .. \quad .. \quad (4)$$

$$\dot{C}_2H_5 + \dot{C}_2H_5 = C_2H_6 + C_2H_4 \quad .. \quad .. \quad (5)$$

$$\dot{C}_2H_5 + \dot{C}_2H_5 = C_4H_{10} \quad .. \quad .. \quad (6)$$

$$\dot{C}H_3 + \dot{C}_2H_5 = CH_4 + C_2H_4 \quad .. \quad .. \quad (7)$$

$$\dot{C}H_3 + \dot{C}_2H_5 = C_3H_8 \quad .. \quad .. \quad (8)$$

Daar bestaan geen sekerheid oor die verdere reaksies van die 3-keto-butielradikaal nie. Die volgende reaksies[5] is voorgestel:

$$CH_3COC_2H_4 + CH_3 = CH_3COC_3H_7 \quad .. \quad .. \quad (9)$$

$$2\,CH_3COC_2H_4 = (CH_3COC_2H_4)_2 \quad .. \quad .. \quad (10)$$

$$CH_3COC_2H_4 + C_2H_5 = CH_3COC_4H_9 \quad .. \quad .. \quad (11)$$

$$CH_3COC_2H_4 = CH_3 + CH_3CHCO \quad .. \quad .. \quad (12)$$

$$CH_3COC_2H_4 = CH_3 + CO + C_2H_4 \quad .. \quad .. \quad (13)$$

In die onderstaande ondersoek word eksperimentele gegewens verstrek wat reaksies (1), (2), . . . (10) ondersteun.

EKSPERIMENTELE BESONDERHEDE EN RESULTATE

Die apparaat wat in hierdie ondersoek gebruik is, is in 'n vorige artikel beskryf[6].

Metieletielketoon (Merck, reinst) is gesuiwer deur herhaalde fraksionele distillasie totdat die massaspektrometriese kraakpatroon onveranderd gebly het. Hierna is die metieletielketoon oor anhidriese natriumsulfaat in 'n donker plek bewaar. Monsters van die metieletielketoon is onderwerp aan die volle straling van 'n hoë-druk kwiklamp (Zeiss VZ Dr Hg 200).

Eksperimente is uitgevoer om die invloed van die reaksietemperatuur, aanvangsdruk van die ketoon en die bestralingstyd op die samestelling van die reaksieprodukte na te gaan. In elke geval is die monsters van die gasmengsel in die reaksiefles sonder verdere behandeling met behulp van 'n massaspektrometer ontleed. Die resultate word in Tabelle I, II en III weergegee. Die volgende simbole vir die vormingsnelhede R, in molekules $cm^{-3}sek^{-1} \times 10^{-14}$, word gebruik:

M : CH_4; E : C_2H_6; En : C_2H_4; P : C_3H_8; B : C_4H_{10};

Mpk : $CH_3COCH_2CH_2CH_3$; Do: $(CH_3COC_2H_4)_2$

[K] : konsentrasie van metieletielketoon in molekules $cm^{-3} \times 10^{-18}$

Eks. nr. : eksperimentnommer

TABEL I

Fotolise van metieletielketoon by verskillende temperature

Aanvangsdruk: 100 mm
Bestralingstyd: 300 sekondes

Eks. nr.	Temp. °C	[K]	R_{CO}	R_M	R_E	R_{En}	R_P	R_R	R_{Mpk}	R_{Do}
1	298	1·69	7·9	3·80	1·80	0·31	0·71	0·48	0·50	2·24
2	285	1·73	8·1	3·50	1·72	0·26	0·98	0·70	0·48	2·03
3	263	1·80	8·1	3·47	1·74	0·31	1·26	0·78	0·45	1·92
4	241	1·88	8·1	2·96	1·66	0·22	1·62	1·08	0·37	1·67
5	221	1·96	8·0	2·47	1·60	0·20	1·65	1·18	0·58	1·30

TABEL II

Fotolise van metieletielketoon by verskillende aanvangsdrukke

Temperatuur: 281°C
Bestralingstyd: 300 sekondes

Eks. nr.	[K]	R_{CO}	R_M	R_E	R_{En}	R_P	R_B	R_{Mpk}	R_{Do}
6	1·78	8·5	3·40	1·90	0·29	1·52	1·10	0·58	1·91
7	1·45	8·3	3·10	1·58	0·26	1·42	1·03	0·57	1·63
8	1·19	6·3	2·75	1·40	0·18	1·10	0·94	0·55	1·50
9	0·80	4·7	1·90	1·00	0·13	0·94	0·61	0·45	0·95
10	0·48	2·8	0·96	0·63	0·10	0·66	0·38	0·21	0·47

TABEL III

Fotolise van metieletielketoon vir verskillende bestralingstye

Temperatuur: 280°C
Aanvangsdruk: 100 mm

Eks. nr.	Sek.	[K]	R_{CO}	R_M	R_E	R_{En}	R_P	R_B	R_{Mpk}	R_{Do}
1	300	1·62	7·6	3·5	2·05	0·35	1·46	0·99	0·64	1·96
12	600	1·54	7·7	2·8	1·64	0·33	1·32	0·75	0·53	1·37

Die noukeurigheid van die analitiese data in Tabelle I, II en III varieer van stof tot stof, maar in die meeste gevalle kan dit aanvaar word dat die fout nie groter is as 10% nie.

Die direkte bepaling van die 2,7-diketo-oktaan, $(CH_3COCH_2CH_2)_2$, was nie moontlik nie, omdat dit in die kouer dele van die apparaat kondenseer. Derhalwe is gebruik gemaak van 'n indirekte metode vir die bepaling, wat hieronder verduidelik word.

BESPREKING

Op grond van die resultate van vorige navorsers[5], en van die produkte wat in hierdie ondersoek waargeneem is, sal reaksies (1), (2), . . . (10) as basis in hierdie bespreking gebruik word.

Indien k_1, k_2, . . . k_{10} die onderskeie snelheidskonstantes voorstel, kan die snelheidsvergelykinge vir die waargenome produkte soos volg weergegee word:

$$R_{CH_4} = k_2[\dot{C}H_3][K] + k_7[\dot{C}H_3][\dot{C}_2H_5] \quad .. \quad (a)$$

$$R_{C_2H_6} = k_3[\dot{C}_2H_5][K] + k_4[\dot{C}H_3]^2 + k_5[\dot{C}_2H_5] \quad .. \quad (b)$$

$$R_{C_2H_4} = k_5[\dot{C}_2H_5]^2 + k_7[\dot{C}H_3][\dot{C}_2H_5] \quad .. \quad (c)$$

$$R_{C_3H_8} = k_8[\dot{C}H_3][\dot{C}_2H_5] \quad .. \quad (d)$$

$$R_{C_4H_{10}} = k_6[\dot{C}_2H_5]^2 \quad .. \quad (e)$$

$$R_{CH_3COC_3H_7} = k_9[\dot{C}H_3][CH_3CO\dot{C}_2H_4] \quad .. \quad (f)$$

$$R_{(CH_3COC_2H_4)_2} = k_{10}[CH_3CO\dot{C}_2H_4]^2 \quad .. \quad (g)$$

Met behulp van hierdie vergelykings kan die volgende verhoudings afgelei word:

$$k_7/k_8 = [R_{En} - R_B k_5/k_6]/R_P \quad .. \quad (i)$$

$$k_2 k_6^{\frac{1}{2}}/k_8 = [R_M - R_P k_7/k_8]\, R_B^{\frac{1}{2}}/R_P[K] \quad .. \quad (ii)$$

$$k_3/k_8^{\frac{1}{2}} = [R_E - R_P^2 k_4 k_6/k_8^2\, R_B - R_B k_5/k_6]/R_B^{\frac{1}{2}}[K] \quad .. \quad (iii)$$

$$k_2 k_{10}^{\frac{1}{2}}/k_9 = [R_M - R_P k_7/k_8]\, R_{Do}^{\frac{1}{2}}/R_{Mpk}[K] \quad .. \quad (iv)$$

Die vormingsnelheid van die 2,7-diketo-oktaan, $R_{(CH_3COC_2H_4)_2}$, of R_{Do} soos dit in die Tabelle I, II en III aangegee is, is met behulp van die volgende vergelyking bereken:

$$R_{Do} = R_{(CH_3COC_2H_4)_2} = \tfrac{1}{2}(r_2 + r_3 - r_9)$$

waarin r_2, r_3 en r_9 die snelhede van die reaksies (2), (3) en (9) onderskeidelik is. Hierdie snelhede kan met behulp van die omskrewe simbole soos volg bereken word:

$$r_2 = R_M - R_P \times k_7/k_8$$

$$r_3 = R_E - R_P^2 \times k_4 k_6/k_8^2 \times R_B - R_B k_5/k_6$$

$$r_9 = R_{Mpk}$$

Teneinde die data van Tabelle I, II en III te gebruik om die verhoudings (i), (ii), (iii) en (iv) te bereken, is dit nodig om die waardes te weet van die konstante verhoudings k_5/k_6 en $k_8/k_4^{\frac{1}{2}}k_6^{\frac{1}{2}}$. Hierdie waardes is in vorige ondersoeke bepaal, nl. 0.125 en 1.84.[4]

In Tabelle IV en V word die eksperimentele waardes vir die verhoudinge (i), (ii), (iii) en (iv) opgesom.

TABEL IV

Die eksperimentele waardes vir die verhoudinge (i), (ii), (iii) en (iv) by verskillende temperature

Eks. nr.	Temp. °C	k_7/k_8	$k_2k_6^{\frac{1}{2}}/k_8$	$k_3/k_8^{\frac{1}{2}}$	$k_2 k_{10}^{\frac{1}{2}}/k_9$
1	298	(0·35)	2·05	1·23	6·27
2	285	0·17	1·65	0·84	5·50
3	263	0·17	1·27	0·75	5·00
4	241	0·05	1·01	0·42	3·94
5	221	0·03	0·81	0·36	2·30

In die berekening van die verhouding $k_2k_{10}^{\frac{1}{2}}/k_9$ is die gemiddelde waarde van 0·50 molekules cm^{-3} $sek^{-1} \times 10^{-14}$ geneem vir R_{Mpk} aangesien die relatiewe groote foute in hierdie snelheid andersinds 'n groot afwykende invloed uitoefen.

Die gegewens van Tabel IV kan gebruik word om Fig. 1, 2 en 3 te teken. In elke geval word die logaritme van die verhoudinge $k_2k_6^{\frac{1}{2}}/k_8$, $k_3/k_8^{\frac{1}{2}}$ en $k_2k_{10}^{\frac{1}{2}}/k_9$ onderskeidlik teen die resiproke van die absolute temperatuur gestip. Die volgende gevolgtrekkinge kan gemaak word:

TABLE V

Die eksperimentele waardes vir die verhoudinge (i), (ii), (iii) en (iv) by 'n bepaalde temperatuur, 280°-281° C

nr. Eks.	k_7/k_8	$k_2k_6^{\frac{1}{2}}/k_8$	$k_3/k_6^{\frac{1}{2}}$	$k_2k_{10}^{\frac{1}{2}}/k_9$
6	0·10	1·23	0·60	4·2
7	0·09	1·33	0·54	4·2
8	0·005	1·89	0·72	4·8
9	0·05	1·86	0·78	5·0
10	0·08	1·70	0·77	6·0
11	0·15	1·36	0·81	5·7
12	0·18	0·98	0·52	4·0

(i) Die verhoudinge $k_2k_6^{\frac{1}{2}}/k_8$, $k_3/k_6^{\frac{1}{2}}$ en $k_2k_{10}^{\frac{1}{2}}/k_9$ bly, binne die eksperimentele fout, konstant by 'n bepaalde temperatuur, en hulle logaritmes verander liniêr met die resiproke van die absolute temperatuur.

(ii) Die verhouding k_7/k_8 bly konstant oor hierdie temperatuurgebied, binne die eksperimentele fout.

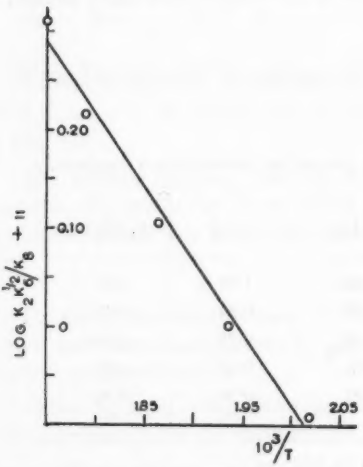

FIG. 1—Log $k_2k_6^{\frac{1}{2}}/k_8$ teenoor I/T gestip

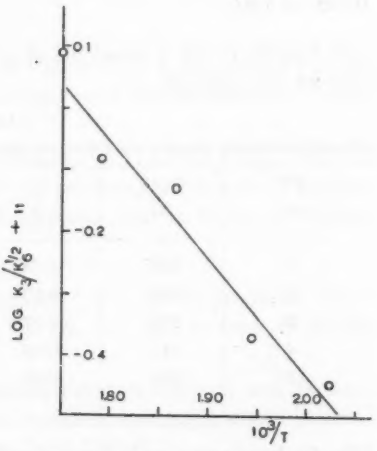

FIG. 2—Log $k_3/k_6^{\frac{1}{2}}$ teenoor I/T gestip

Hierdie gevolgtrekkinge bevestig die reaksieskema (1), (2), . . . (10) waarin reaksies (4), (5), . . . (10) almal vry radikaal-kombinasies of -ontbindinge is, met aktiveringsenergië E_4, E_5. . . . E_{10} almal bykans nul. Daarteenoor is die aktiveringsenergië van die waterstofonttrekkinge in reaksies (2) en (3) nie nul nie. Uit die hellinge van die Arrhenius-grafieke, Fig. 1, 2 en 3, volg:

$E_2 + \frac{1}{2}E_6 - E_8 = 6{\cdot}8$ kkal per mol

$E_2 + \frac{1}{2}E_{10} - E_9 = 7{\cdot}1$ kkal per mol

$E_3 - \frac{1}{2}E_6 = 8{\cdot}7$ kkal per mol

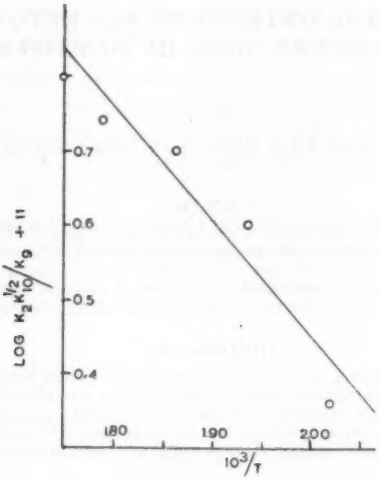

FIG. 3—Log $k_2k_{10}^{\frac{1}{2}}/k_9$ teenoor I/T gestip

Omdat $E_4, E_5 \ldots E_{10}$ almal bykans nul is, is $E_2 = 6{\cdot}8$ en 7·1 (Ausloos en Steacle[5], 7·4) en $E_3 = 8{\cdot}7$ (Ausloos en Steacie[5], 8·0) kkal per mol.

Vir die verhouding van die disproporsionasie tot die kombinasie van die metiel- en etielradikale, nl. k_7/k_8, word in die literatuur[5, 7] variërende waardes aangetref. Hiermee stem die gemiddelde waarde 0·1, uit Tabelle IV en V, redelik goed ooreen.

Dank word uitgespreek teenoor die Wetenskaplike Nywerheidsnavorsingsraad vir die gebruik van 'n massaspektrometer en die toekenning van 'n beurs aan een van die skrywers (J.A. v.d. B.); aan African Explosives and Chemical Industries Ltd. vir 'n navorsingstoekenning aan die ander skrywer (V.P.); en aan Prof. dr. L. J. le Roux vir sy belangsteiling in hierdie werk.

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DIE FOTOLITIESE ONTBINDING VAN KETONE BY HOË TEMPERATURE. DEEL III. DI-ETIELKETOON

deur

J. A. VAN DEN BERG en V. PRETORIUS

SUMMARY

The photolysis of diethyl ketone has been studied in the range 220-310°C using a mass spectrometer. The reaction products have been quantitatively estimated by direct analysis as carbon monoxide, n-butane, ethylene, ethane and ethyl butyl ketone. The presence of the diketone $(C_2H_4COC_2H_5)_2$ has been indirectly confirmed. The observed reaction products and kinetics of the decomposition have been accounted for by a series of free radical reactions.

OPSOMMING

Die fotolise van di-etielketoon, oor die gebied 220-310°C, is met behulp van 'n massaspektrometer ondersoek. Die reaksieprodukte wat op hierdie wyse kwantitatief vasgestel is, is koolstofmonoksied, n-butaan, etileen, etaan en etielbutielketoon. Die teenwoordigheid van die diketoon $(C_2H_4COC_2H_5)_2$ is op indirekte wyse bevestig. Die ontstaan van die waargenome produkte en die kinetika van die ontbinding word verklaar deur 'n reeks vry radikaalreaksies.

INLEIDING

Die fotolise van di-etielketoon is die afgelope jare 'n aantal kere ondersoek[1,2,3,4]. Per molekul di-etielketoon fotochemies ontbind, ontstaan een molekul koolstofmonoksied, indien die temperatuur hoog genoeg is[1]. Die vernaamste produkte is koolstofmonoksied, etileen, etaan en n-butaan. Geringe hoeveelhede metielketeen, asetaldehied en waterstof, wat toeneem by 400°C, en hoër, is vasgestel[5].

Die volgende vry radikaal-reaksieskema vir die fotolise van di-etielketoon is voorgestel[1,3]:

$$C_2H_5COC_2H_5 + lig = 2\dot{C}_2H_5 + CO \quad .. \quad .. \quad .. \quad (1)$$

$$2\dot{C}_2H_5 = C_4H_{10} \quad .. \quad .. \quad .. \quad (2)$$

$$2\dot{C}_2H_5 = C_2H_4 + C_2H_6 \quad .. \quad .. \quad .. \quad (3)$$

$$\dot{C}_2H_5 + C_2H_5COC_2H_5 = C_2H_6 + \dot{C}_2H_4COC_2H_5 \quad .. \quad .. \quad .. \quad (4)$$

$$\dot{C}_2H_5 + \dot{C}_2H_4COC_2H_5 = C_4H_7COC_2H_5 \quad .. \quad .. \quad .. \quad (5)$$

$$2\,\dot{C}_2H_4COC_2H_5 = (C_2H_4COC_2H_5)_2 \quad .. \quad .. \quad .. \quad (6)$$

Omdat slegs koolstofmonoksied, etileen, etaan en n-butaan totnogtoe kwantitatief bepaal is, kan alleen reaksies (1) . . . (4) van die bostaande skema met sekerheid aanvaar word. Die reaksies (5) en (6) is bygevoeg[3] na analogie van die fotolise van asetoon, maar daar bestaan geen direkte bewys hiervoor nie. In die onderstaande ondersoek word direkte bewys vir (5) gelewer en indirekte bewys vir (6) aangevoer.

EKSPERIMENTELE BESONDERHEDE EN RESULTATE

Di-etielketoon (Merck, reinst) is deur fraksionele distillasie gesuiwer deur 'n kolom met 'n skeidingsdoeltreffendheid van 20 teoretiese plate. Die suiwer produk is oor anhidriese natriumsulfaat in 'n donker fles bewaar. Die fotolitiese ontbinding is in 'n apparaat uitgevoer wat in 'n vorige artikel[6] beskryf is. Die volle bestraling van 'n hoë druk kwiklamp (Zeiss, VZ Dr Hg 200) is gebruik.

Drie reekse eksperimente is uitgevoer by sodanige kondisies dat telkens net één van die veranderlike faktore temperatuur, druk en bestralingstyd verander word, waardeur die interpretasie van die resultate vergemaklik word. Die resultate van die drie reekse word in Tabelle I, II en III saamgevat. Die volgende simbole word in die tabelle en die verdere bespreking gebruik:

D : konsentrasie van di-etielketoon in molekule per $cm^3 \times 10^{-18}$
R : vormingsnelheid in molekule per cm^3 per sel $\times 10^{-14}$
B : C_4H_{10}
E : C_2H_6
En : C_2H_4
Ebk : $C_4H_9COC_2H_5$
Dik : $(C_2H_4COC_2H_5)_2$
Eks. nr. : Eksperimentnommer

TABEL I

Die fotolise van di-etielketoon by verskillende temperature

Aanvangsdruk: 30 mm
Bestralingstyd: 360 sek

Eks. nr.	Temp. °K	[D]	R_{CO}	R_B	R_E	R_{En}	R_{Ebk}	R_{Dik}
1	570	0·43	3·6	1·69	2·01	0·23	0·20	0·79
2	556	0·45	3·5	2·03	1·69	0·30	0·22	0·58
3	535	0·47	3·4	2·16	1·41	0·26	0·20	0·47
4	514	0·49	3·4	2·33	1·25	0·33	0·22	0·35
5	493	0·52	3·3	2·49	0·93	0·27	0·13	0·28

TABEL II

Die fotolise van di-etielketoon by verskillende aanvangsdrukke

Bestralingstyd: 300 sek
Temperatuur: 265°C

Eks. nr.	[D]	R_{CO}	R_B	R_E	R_{En}	R_{Ebk}	R_{Dik}
6	0·227	2·40	1·54	0·94	0·31	0·11	0·27
7	0·336	2·88	1·70	1·14	0·26	0·10	0·39
8	0·354	3·06	2·0	1·35	0·37	0·10	0·44
9	0·482	3·25	2·13	1·50	0·23	0·22	0·53

TABEL III

Die fotolise van di-etielketoon vir verskillende bestralingstye

Eks. nr.	Temp. °K	Sek.	[D]	R_{CO}	R_B	R_E	R_{En}	R_{Ebk}	R_{Dik}
10	264·5	180	0·511	3·0	1·87	1·24	0·11	0·13	0·50
11	264·5	240	0·500	3·0	1·91	1·31	0·26	0·19	0·43
12	264·5	300	0·477	3·0	1·92	1·35	0·26	0·14	0·48
13	278	600	0·444	3·0	1·89	1·30	0·28	0·10	0·46

Die noukeurigheid van die aangegewe snelhede is ongeveer 10%. Die bepaling van die etileen is heelwat minder akkuraat aangesien die berekening berus op klein verskille tussen betreklike groot hoeveelhede. Die klein massaspektrometriese piekhoogtes by massagetalle 85 en 114 vir etielbutielketoon het die noukeurige bepaling van hierdie ketoon bemoeilik.

Die diketoon $(C_2H_4COC_2H_5)_2$, wat nie vlugtig genoeg is om saam met die ander produkte in die gasfase na die massaspektrometer oorgedra te word nie, en spesiale apparaat sou vereis om bepaal te word, is indirek bereken uit die snelhede waarmee etaan, etileen en etielbutielketoon gevorm word:

$$R_{(C_2H_4COC_2H_5)_2} = \tfrac{1}{2}(R_{C_2H_6} - R_{C_2H_4} - R_{Ebk}).$$

BESPREKING

Op grond van die waargenome reaksieprodukte en die gevolgtrekkings van vorige ondersoekers word reaksies (1), . . . (6) van die bostaande skema aanvaar as die uitgangspunt van hierdie bespreking. Met behulp van die resultate vervat in Tabelle I, II en III, kan die geldigheid van hierdie uitgangspunt getoets word.

Die massa-balans met betrekking tot die etielradikale, m, word gegee deur die volgende vergelyking:

$$m = (R_{C_4H_{10}} + \tfrac{1}{2}R_{C_2H_4} + \tfrac{1}{2}R_{C_2H_6} + \tfrac{1}{2}R_{Ebk})/R_{CO} = 1 \quad .. \quad .. \quad .. \quad (a)$$

Die waardes van m verkry uit die eksperimentele gegewens in Tabelle I, II en III, word in Tabel IV opgesom:

TABLE IV

Die massa-balans m bereken uit vergelyking (a)

Eks. nr.	1	2	3	4	5	6	7	8	9	10	11	12	13
m	·81	·89	·91	·94	·95	·92	·85	·95	·96	·87	·92	·93	·91

Die tabel dui aan dat sowat 95% van die etielradikale volgens reaksies (1), (2) . . . (6) opgebruik word.

Verskillende toetse vir die reaksieskema (1), (2), (3) . . . (6) kan met behulp van die snelheidsvergelykings aangelê word. Indien die snelheidskonstantes van reaksies (1), (2), . . . (6) deur k_1, k_2, ... k_6 onderskeidelik gegee word, geld:

$$R_{C_4H_{10}} = k_2[\dot{C}_2H_5]^2 \quad \ldots\ldots\ldots \quad (b)$$

$$R_{C_2H_4} = k_3[\dot{C}_2H_5]^2 \quad \ldots\ldots\ldots \quad (c)$$

$$R_{C_2H_6} = k_3[\dot{C}_2H_5]^2 + k_4[\dot{C}_2H_5][D] \quad \ldots\ldots\ldots \quad (d)$$

$$= R_{C_2H_4} + R^{\frac{1}{2}}_{C_4H_{10}} \cdot [D] \cdot k_4/k_2^{\frac{1}{2}} \quad \ldots\ldots\ldots \quad (e)$$

$$R_{C_2H_5COC_4H_9} = k_5[\dot{C}_2H_5][\dot{C}_2H_4COC_2H_5] \quad \ldots\ldots\ldots \quad (f)$$

$$R_{(C_2H_4COC_2H_5)_2} = k_6[\dot{C}_2H_4COC_2H_5]^2 \quad \ldots\ldots\ldots \quad (g)$$

Uit die vergelykinge (b), (c), . . . (g) kan die volgende verhoudings afgelei word:

$$k_4/k_2^{\frac{1}{2}} = (R_{C_2H_6} - R_{C_2H_4})/R^{\frac{1}{2}}_{C_4H_{10}} \cdot [D] \quad \ldots\ldots\ldots \quad (h)$$

$$k_4/k_3^{\frac{1}{2}} = (R_{C_2H_6} - R_{C_2H_4})/R^{\frac{1}{2}}_{C_2H_4} \cdot [D] \quad \ldots\ldots\ldots \quad (i)$$

$$k_5/k_2k_6 = R^2_{C_2H_5COC_4H_9}/\tfrac{1}{2}(R_{C_2H_6} - R_{C_2H_4} - R_{C_2H_5COC_4H_9})R_{C_4H_{10}} \quad \ldots \quad (j)$$

$$k_3/k_2 = R_{C_2H_4}/R_{C_4H_{10}} \quad \ldots\ldots\ldots \quad (k)$$

Die data in tabelle I, II en III is in vergelykinge (h), . . . (k) gesubstitueer en die resultate opgesom in Tabelle V en VI.

TABLE V

Eksperimentele waardes van die verhoudinge (h), (i), (j) en (k) by verskillende temperature

Eks. nr.	Temp. °K	$k_4\ k/k_2^{\frac{1}{2}}$	$k_4/k_3^{\frac{1}{2}}$	k_5^2/k_2k_6	k_3/k_2
1	579	3·17	8·6	0·030	0·136
2	556	2·17	5·57	0·041	0·148
3	535	1·65	4·75	0·039	0·120
4	514	1·23	3·29	0·059	0·145
5	493	0·081	2·24	0·025	0·109

TABEL VI

Eksperimentele waardes van die verhoudinge (h), (i), (j) en (k) by 'n vaste temperatuur, 265°C

Eks. nr.	$k_4/k_2^{\frac{1}{2}}$	$k_4/k_3^{\frac{1}{2}}$	$k_5^2/k_2\,k_6$	k_3/k_2
6	2·03	5·2	0·023	0·153
7	1·96	4·7	0·015	0·185
8	1·81	5·5	0·011	0·108
9	1·81	5·5	0·043	0·115
10	1·63	6·7	0·018	0·060
11	1·52	4·2	0·044	0·136
12	1·65	4·6	0·022	0·135

Die logaritmes van die verhoudinge (h) en (i) is uit Tabel V teen die resiproke van die absolute temperatuur gestip, soos aangedui in Fig. 1 en 2.

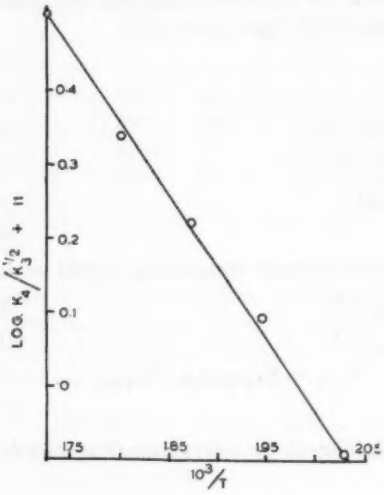

FIG. 1—Log $k_4/k_3^{\frac{1}{2}}$ gestip teen I/T

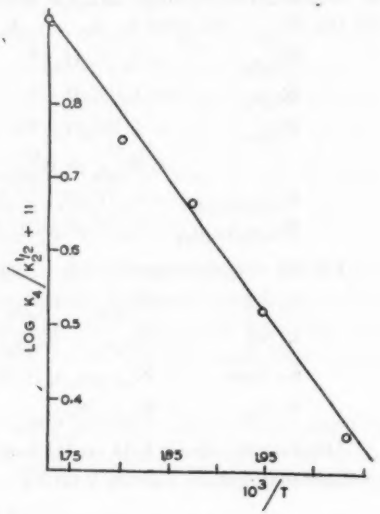

FIG. 2—Log $k_4/k_2^{\frac{1}{2}}$ gestip teen I/T

Die Tabelle V en VI, en die Fig. 1 en 2 toon aan dat, binne die eksperimentele fout, die verhoudinge $k_4/k_2^{\frac{1}{2}}$ en $k_4/k_3^{\frac{1}{2}}$ konstant bly by 'n bepaalde temperatuur, en dat hulle logaritmes liniêr verander met die resiproke van die absolute temperatuur. Daarenteen, bly die verhoudinge k_3/k_2 en k_5^2/k_2k_6 oor hierdie temperatuurgebied konstant, binne die eksperimentele fout.

Hierdie gevolgtrekkinge bevestig die reaksieskema (1), (2), (3) . . . (6), waarin reaksies (2), (3), (5) en (6) vry radikaal-kombinasies is met aktiveringsenergië E_2, E_3, E_5 en E_6 van orde nul. Die snelheidskonstantes k_2, k_3, k_5 en k_6 is dus prakties onafhanklik van die temperatuur. Die onafhanklikheid van temperatuur van die verhoudinge k_3/k_2 en k_5^2/k_2k_6 word daardeur verklaar. Dit bewys die geldigheid van reaksies (5) en (6).

Die aktiveringsenergie E_4 vir die waterstofonttrekking in reaksie (4) is egter nie nul nie. Die temperatuurafhanklikheid van die verhoudinge $k_4/k_2^{\frac{1}{2}}$ en $k_4/k_3^{\frac{1}{2}}$ stem hiermee ooreen. Uit die helling van die Arrhenius-grafiek, Fig. 1, word bevind: $E_4 - \frac{1}{2}E_2 = 7{\cdot}8$ kkal per mol. Fig. 2 lewer $E_4 - \frac{1}{2}E_3 = 8{\cdot}1$ kkal per mol. Die resultaat $E_4 = 8{\cdot}0 \pm 0{\cdot}2$ kkal per mol, stem beter met dié van Steacie en sy medewerkers[3, 7] ooreen, nl. 7·5 en 7·6, as met dié van Dorfman en Sheldon[1], nl. 4·1.

Dank word uitgespreek teenoor die Wetenskaplike Nywerheidsnavorsingsraad vir die gebruik van 'n massaspektrometer en die toekenning van 'n beurs aan die

een skrywer (J. A. v.d. B.); teenoor African Explosives and Chemical Industries Ltd. vir 'n navorsingstoekenning aan die ander skrywer (V.P.); en teenoor Prof. L. J. Le Roux, van die Dept. Fisiese Chemie, Universiteit Pretoria, vir sy belangstelling in die werk.

Departement Fisiese Chemie,
Universiteit Pretoria.

Ontvang 20 *Mei*, 1959.

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DIE PIROLISE VAN DITERSIÊRE BUTIELPEROKSIED IN DIE GASFASE

deur

F. BESSINGER en V. PRETORIUS

SUMMARY

The products of the thermal decomposition of ditertiarybutyl peroxide at 160°C in the gas phase have been identified by means of mass spectrometric analysis. A reaction scheme to account for the observed products has been put forward and the activation energies of a number of the elementary reactions have been estimated.

OPSOMMING

Die produkte gevorm gedurende die termiese ontbinding van ditersiêre butielperoksied by 160° C in die gasfase is d.m.v. 'n massaspektrometer ontleed. 'n Reaksieskema om die ontstaan van die waargenome produkte te verklaar word voorgestel en die aktiveringsenergieë van 'n aantal van die elementêre reaksies is bereken.

INLEIDING

Die primêre stap in die pirolitiese ontbinding van ditersiêre butielperoksied in die gasfase is al met 'n groot mate van sekerheid vasgestel[1,2] as die breking van die peroksiedbinding gevolg deur die ontbinding van die gevormde butoksieradikaal om asetoon en 'n metielradikaal te lewer:

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2\,(CH_3)_3CO\cdot \quad .. \quad .. \quad .. \quad (1)$$

$$(CH_3)_3CO\cdot \longrightarrow CH_3COCH_3 + \cdot CH_3 \quad .. \quad .. \quad .. \quad (2)$$

In 'n gepakte reaksiefles is slegs asetoon en etaan waargeneem as produkte en gevolglik is dit redelik seker dat die verdere reaksies van die metielradikale beperk is tot bimolekulêre herverbinding nl.

$$\cdot CH_3 + \cdot CH_3 \longrightarrow C_2H_6 \quad .. \quad .. \quad .. \quad (3)$$

In 'n ongepakte reaksiefles, egter, is metieletielketoon en metaan sowel as asetoon en etaan waargeneem, en die volgende reaksies is voorgestel[3,6] om die ontstaan van hierdie produkte te verklaar:

$$\cdot CH_3 + (CH_3)_3COOC(CH_3)_3 \longrightarrow CH_4 + \cdot CH_2(CH_3)_2COOC(CH_3)_3 \quad .. \quad (4)$$

$$\cdot CH_2(CH_3)_2COOC(CH_3)_3 \longrightarrow (CH_3)_2\overset{\overset{O}{\diagup\diagdown}}{C}\!-\!CH_2 + CH_3COCH_3 + \dot{C}H_3 \quad (5)$$

$$\cdot CH_3 + CH_3COCH_3 \longrightarrow CH_4 + \cdot CH_2COCH_3 \quad .. \quad .. \quad .. \quad (6)$$

$$\cdot CH_3 + \cdot CH_2COCH_3 \longrightarrow CH_3CH_2COCH_3 \quad .. \quad .. \quad .. \quad (7)$$

Die vasstelling van die teenwoordigheid van die butileenoksied berus op fraksionele distillasie en chemiese analise en met inagneming van die besonder

klein hoeveelheid stof beskikbaar vir die analise kan die geldigheid van reaksie (5) nie met sekerheid aanvaar word nie. Vir die beginstadia is die reaksie homogeen en van die eerste orde[2]. Kettingreaksies is afwesig. Die spoedbepalende stap is die breking van die peroksiedbinding (reaksie (1)) met 'n aktiveringsenergie van 36·0 tot 39·1 kkal/mol[5].

Die doel van die ondersoek wat hier beskryf word was om eerstens die reaksieprodukte te ondersoek met behulp van 'n massaspektrometer om 'n uitspraak te kry op die meganisme en tweedens om die aktiveringsenergieë van die afsonderlike reaksiestappe waar moontlik te bereken.

EKSPERIMENTELE BESONDERHEDE EN RESULTATE

Die apparaat. 'n Skematiese diagram van die apparaat word in Fig. 1 aangetoon. 'n Glas reaksiefles A (*ca.* 250 ml) is by die verlangde temperatuur gehou deur die damp van 'n vloeistof met 'n geskikte kookpunt[7]. Temperatuurbeheer van beter as 0·1°C kon op hierdie wyse verkry word. Die peroksied is in die bol D bewaar. Die hele monsterinlaatsisteem is in 'n kas ingebou wat elektries verhit is. Op hierdie wyse kon gasdrukke van ongeveer 100 mm Hg in die reaksiefles verkry word. Gasdrukke is op 'n Hg-manometer gemeet.

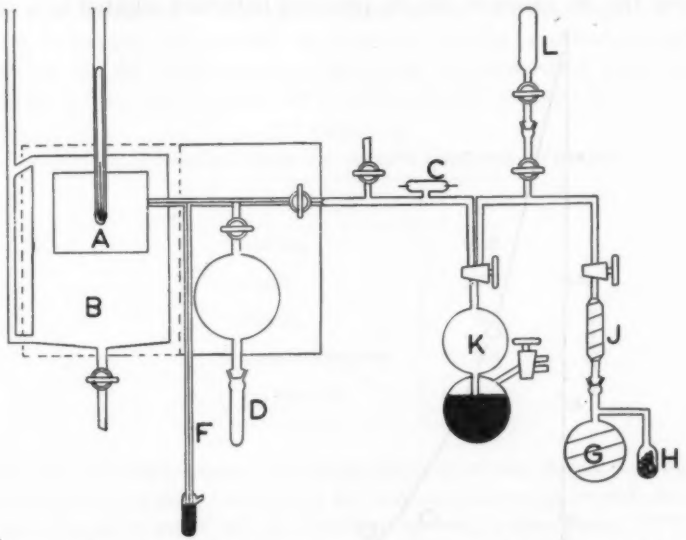

FIG. 1—Skematiese diagram van die apparaat. A—Reaksiefles. B—Oond. C—Ontladingsbuis. D—Peroksied. E—Manometer. G—Natrium en glas wol. H—Natrium. J—Anhidriese natriumsulfaat. K—Toeplerpomp. L—Monsterhouer

Die absorpsiefles G is gebruik vir die verwydering van die ongereageerde peroksied. Natriummetaal H is op die glas wol in G gedistilleer om 'n groot aktiewe opper-

vlakte van die suiwer metaal te lewer. Gasmengsels is in J oor watervrye natriumsulfaat gedroog voordat hulle by G ingelaat is. Die Toeplerpomp K is gebruik om die gasse van een fles na die ander oor te plaas. Gasmonsters is by die uitlaat L verwyder vir analise op die massaspektrometer.

Die apparaat is met 'n meganiese oliepomp en 'n diffusiepomp uitgepomp. 'n Ontladingsbuis C het 'n rowwe aanduidiging gegee van die lugleegte wat bereik is.

Die ditersiêre butielperoksied is berei volgens die metode van Milas en Surgenor[1]. Die suiwerheid van die produk is getoets deur meting van die brekingsindeks.

$n_D^{25°}C$ (gegee)[1] = 1·3863
$n_D^{25°}C$ (gevind) = 1·3867

Analise van 'n monster van die peroksied d.m.v. gasverdelingschromatografie het getoon dat dit minstens 99·7% suiwer is.

Die selektiewe absorbsie van ditersiêre butielperoksied. Die analise van die reaksieprodukte is belemmer deur die teenwoordigheid van groot hoeveelhede onontbinde peroksied. Dit is gevind dat natriummetaal die peroksied selektief uit 'n gasmengsel verwyder. Die snelheid van absorpsie van die peroksied word in Fig. 2 aangetoon. Dat die absorpsie van die peroksied inderdaad selektief is, is aangetoon

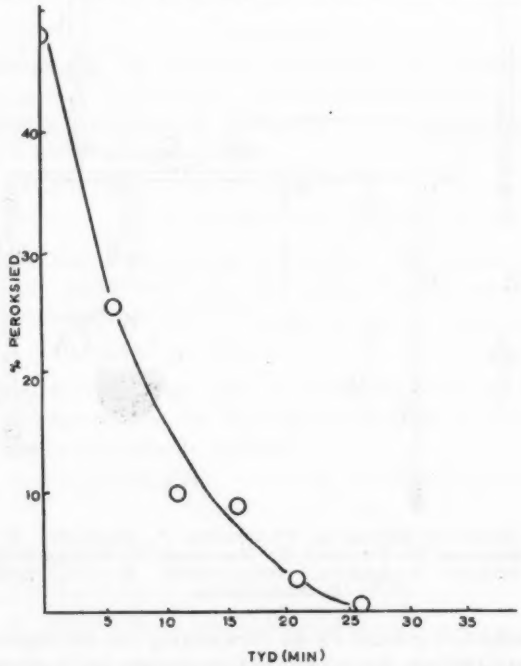

FIG. 2—Die selektiewe absorpsie van ditersiêre butielperoksied

deur 'n mengsel van die peroksied en die belangriker reaksieprodukte voor en na behandeling met natriummetaal te analiseer.

TABEL I

Die selektiewe absorpsie van ditersiêre butielperoksied deur natrium-metaal

	Parsiële druk (mm Hg)	
	absorpsie	
	Voor	Na
Ditersiêre butielperoksied	60·5	1·8
Asetoon	12·0	12·1
Etaan	20·8	20·9
Metieletielketoon	6·7	6·5

Hierdie metode is slegs gebruik om die reaksieprodukte uit te ken. Sodra hulle bekend was kon die analises uitgevoer word sonder om die peroksied te verwyder.

Die reaksieprodukte. Ditersiêre butielperoksied (50 mm druk) is verhit by 160°C vir ses minute, d.w.s. totdat ongeveer 5% van die peroksied ontbind het. Na verwydering van die oorblywende peroksied oor natriummetaal is die gasmengsel op 'n massaspektrometer ontleed. Die resultate verskyn in Tabel II.

TABEL II

Die ontbindingsprodukte van ditersiêre butielperoksied by 160°C

Stof	%
Asetoon	61·8
Etaan	28·9
Metaan	3·3
Metieletielketoon	3·8
ters-Butanol	1·9

Die totale aktiveringsenergie. Die ontbindingsnelheid van die peroksied is gerieflikheidsonthalwe gevolg deur meting van die drukverandering gedurende die gang van die reaksie. Monsters van 25 ml elk is ontbind by temperature tussen 150°C en 180°C. Die aanvangsreaksiesnelhede is verkry vanaf die raaklyne aan die druk-tyd-krommes, Fig. 3. Die resultate word in Tabel III aangegee.

Die logaritmes van die snelhede in Tabel III is gestip teen die resiproke van die absolute temperatuur soos aangedui in Fig. 4. Uit die helling van hierdie kromme is die totale aktiveringsenergie bereken as 35·7 kkal/mol wat goed ooreenstem met die waarde van Szwarc[5].

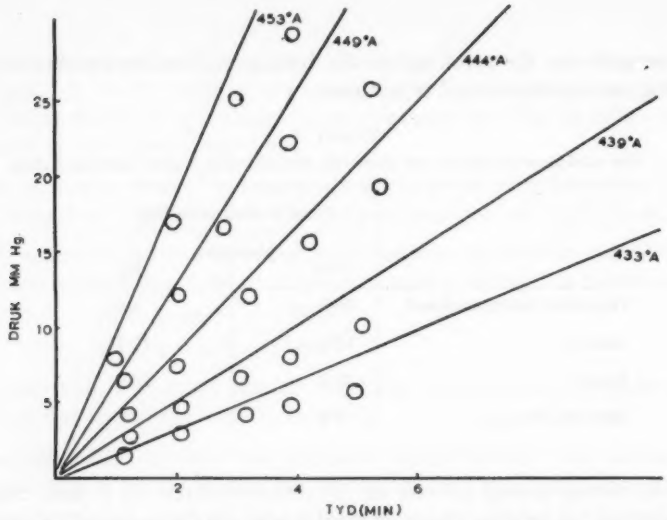

FIG. 3—Die snelheid van die ontbinding by verskillende temperature

TABEL III

Die invloed van temperatuur op die ontbindingsnelheid van ditersiêre butielperoksied

Temp. (A°)	$(1/T) \times 10^4$	Snelheid (mm Hg/min)	log (snelheid) $\times 10^2$
453	22·08	8·63	93·6
449	22·27	6·167	79·01
444	22·52	3·91	59·22
439	22·78	2·372	37·52
433	23·09	1·498	17·52

TABEL IV

Die samestelling van die reaksieprodukte by verskillende temperature

Stof	Snelheid van ontbinding of vorming in mm Hg/min.				
	165°C	169°C	174°C	184°C	188°C
Ditersiêre butielperoksied	2·349	3·263	5·227	12·74	17·52
ters-Butanol	0·2497	0·2763	0·3965	1·371	1·719
Metieletielketoon	0·0415	0·0531	0·0641	0·0868	0·1615
Asetoon	3·911	4·750	6·727	18·68	29·83
Etaan	0·9255	1·195	1·680	4·665	7·364
Metaan	0·1085	0·1645	0·2379	0·5749	0·6175

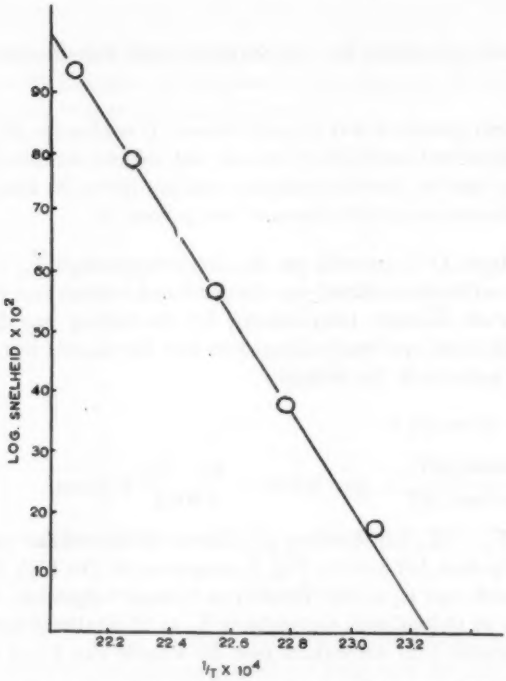

FIG. 4—Die verandering van die ontbindingsnelheid (bereken uit die drukverandering) met temperatuur

Die invloed van temperatuur op die samestelling van die reaksieprodukte. Monsters van 25 ml elk van die peroksied is ontbind by temperature tussen 165°C en 188°C totdat een-derde van die peroksied ontbind het. Monsters van die reaksiemengsel is m.b.v. 'n massaspektrometer in elke geval ontleed. Die resultate word in Tabel IV aangegee.

BESPREKING

Om die waargenome produkte te verklaar word reaksies (1), (2), (3) en (4) van die bogenoemde skema behou. Die vorming van tersiêre butanol kan verklaar word deur die reaksie:

$$(CH_3)_3\dot{C}O + (CH_3)_3COOC(CH_3)_3 \longrightarrow (CH_3)_3COH + \dot{C}H_2(CH_3)_2COOC(CH_3)_3 \qquad (8)$$

Die botsingsfrekwens van hierdie reaksie is relatief groot aangesien die grootste gedeelte van die gas, in die vroeë stadia van die ontbinding, uit die peroksied bestaan.

Die vorming van metieletielketoon via reaksies (6) en (7) kan as onwaarskynlik beskou word in die begin stadium van die ontbinding aangesien die konsentrasie van asetoon te laag sal wees. Op grond hiervan en ook weens die afwesigheid van butileenoksied in die produkte, word reaksie (5) vervang deur:

$$\dot{C}H_2(CH_3)_2COOC(CH_3)_3 \longrightarrow CH_3CH_2COCH_3 + (CH_3)_3\dot{C}O \qquad (9)$$

Die waargenome produkte kan dus verklaar word met die reaksies (1), (2), (3), (4), (8) en (9).

Die hoeveelheid peroksied wat volgens reaksie (1) ontbind is gelyk aan die totale hoeveelheid peroksied wat ontbind het min die wat volgens reaksies (8) en (4) gebruik is. Die ontbinding van die peroksied volgens reaksies (4) en (8) kan gemeet word uit die hoeveelheid metaan en tersiêre butanol wat gevorm is.

Die data in tabel IV is gebruik om die aktiveringsenergie E_1 van reaksie (1) te bereken deur die ontbindingsnelheid van die peroksied volgens reaksie (1) te stip teen die resiproke van die absolute temperatuur. Uit die helling van die kromme is E_1 bereken as 35·5 kkal/mol wat goed ooreenstem met die waarde wat verkry is uit die drukverandering gedurende die reaksie.

Van reaksies (2) en (8) is

$$\log_{10} \frac{\text{d (asetoon)/dT}}{\text{d (t-butanol) /dT}} \times \text{(peroksied)} = \frac{E_8 - E_2}{4{\cdot}606T} + \text{konst.}$$

Die waarde van $E_8 - E_2$ kan bereken word deur die linkerkant van die bostaande vergelyking te stip teen 1/T soos in Fig. 5 aangetoon is. Dit blyk dat $E_8 - E_2 \doteqdot 0$. 'n Benaderde waarde van E_2 is deur Brinton en Volman[8] afgelei nl. 17 ± 3 kkal/mol. Yoffe[9] gee E_2 aan as 14 kkal/mol. Gevolglik is $E_8 \doteqdot 14$ kkal/mol wat binne die perke van die eksperimentele fout ooreenkom met die waarde van Frost en Pearson[6] van 12 kkal/mol.

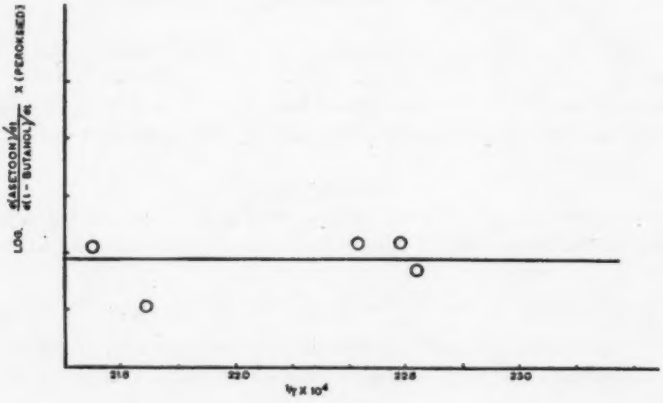

FIG. 5

Van reaksies (4) en (3) is

$$\log_{10} \frac{\text{d (etaan)/dT}}{\text{d (metaan)/dT}} \times \text{(peroksied)}^2 = \frac{2E_4 - E_3}{4{\cdot}606T} + \text{konst.}$$

Die linkerkant van hierdie vergelyking is teen 1/T gestip (Fig. 6) en lewer 'n waarde van $2E_4 - E_3 = 33$ kkal/mol. As aangeneem word dat $E_6 = 0$, is $E_5 = 16{\cdot}5$ kkal/mol. Trotman-Dickenson [10] skat $E_5 = 15$ kkal/mol.

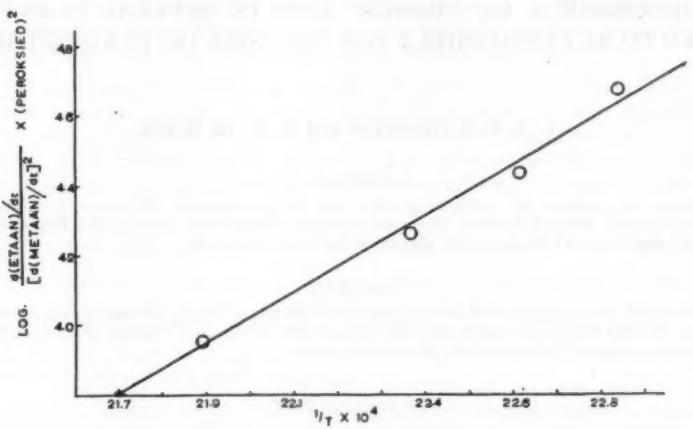

FIG. 6

Dank word uitgespreek teenoor die massaspektrometriese afdeling van die Wetenskaplike Nywerheidsnavorsingsraad vir hulp met die analises. Een van ons (V.P.) wil African Explosives and Chemical Industries Ltd., bedank vir 'n navorsingstoekenning.

Departement Fisiese Chemie,
Universiteit Pretoria.

Ontvang 15 *April*, 1959.

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THE OCCURRENCE OF URSOLIC ACID IN SEVERAL PLANTS REPORTED TO BE RESPONSIBLE FOR "GOUSIEKTE" IN SOUTH AFRICA

by

L. A. P. ANDERSON and W. T. DE KOCK

OPSOMMING

Ursolsuur is geïsoleer uit verskeie spesies van die plantfamilie *Rubiaceae*, naamlik, *Pachystigma pygmaeum*, *Pavetta harbori*, *Pygmaeothamnus zeyheri* var. *zeyheri* en *Pygmaeothamnus zeyheri* var. *rogersii*, wat vermoedelik gousiekte by vee veroorsaak.

SUMMARY

Ursolic acid was isolated from several species of the plant family *Rubiaceae, viz., Pachystigma pygmaeum, Pavetta harbori, Pygmaeothamnus zeyheri* var. *zeyheri* and *Pygmaeothamnus zeyheri* var. *rogersii* which produce "gousiekte" in sheep and cattle.

INTRODUCTION

Gousiekte is a disease causing heavy annual losses among sheep and cattle in the Transvaal and some areas of Natal. The disease mainly effects the heart and derives its name from the fact that it causes instantaneous death through heart failure after a latent period of about thirty-seven days. Feeding experiments[1,2] proved that the gousiektebossie, *Pachystigma pygmaeum* (Schl.) Robyns and *Pavetta harbori* (fam. *Rubiaceae*) were responsible for the disease. Veldsman[3] isolated four non-toxic crystalline principles from the former plant, *viz.*, mannitol, a phytosterol, a lactone and a flavone glycoside since identified as rutin[4].

Serious outbreaks of the disease during the past few years prompted the National Chemical Research Laboratory and the Division of Veterinary Services of the Department of Agriculture, Onderstepoort, to embark on a collaborative programme of chemical and chemical pathological research on gousiekte.

The chemical investigation of the leaves of the above two plants and of the leaves of the hairy "goorappel," *Pygmaeothamnus zeyheri* var. *rogersii* (fam. *Rubiaceae*) and the smooth "goorappel", *Pygmaeothamnus zeyheri* var. *zeyheri* (fam. *Rubiaceae*) resulted in the isolation of the triterpenoid acid, ursolic acid. In *Pavetta harbori* yields of 0·25-0·4% of ursolic acid (based on dry weight) were obtained, whereas in the others the yield varied from 0·05-0·15%. The roots appeared to contain no ursolic acid. Physiological tests with ursolic acid are being carried out by the Division of Veterinary Services, Onderstepoort, and will be reported elsewhere in due course.

EXPERIMENTAL

Unless specified to the contrary $[\alpha]_D$ and infrared spectra were determined in chloroform solutions. Infrared spectra were obtained on a Perkin-Elmer Infracord Model 137 spectrophotometer. All m.p.s. are corrected.

Isolation of ursolic acid. Dried, ground leaves of the above mentioned plants were extracted exhaustively with cold 96% ethanol (3 × 2l./kg) and the extract, after concentration, kept in the cold room overnight. The crude, tarry, green precipi-

tate was filtered off and extracted several times with hexane to remove fats and chlorophyll. The undissolved residue was taken up in hot 96% ethanol, treated with charcoal, filtered and concentrated to give a crude, straw-coloured, crystalline product which had a slightly sweet taste suggesting the presence of a sugar. The sugar was extracted with hot water, crystallised from abs. ethanol and identified as mannitol by m.p. and mixed m.p. 166° and paper chromatography (system: ethanol-butanol-water, 20:1:3, sprayed with ammoniacal silver nitrate, R_F 0·37).

The water insoluble residue was recrystallised several times from 96% ethanol to give fine, colourless needles of ursolic acid, m.p. and mixed m.p. 284-286°, $[\alpha]_D$ +70·6° (c, 0·5% in 96% EtOH) [Found: C, 79·0; H, 10·5. Calc. for $C_{30}H_{48}O_3$: C, 78·9; H, 10·6%]. An authentic sample of ursolic acid was prepared from the leaves of *Psidium guaijava*[5], and in addition a sample was supplied by Prof. R. Tschesche.

Ursolic acid methyl ester, prepared with diazomethane and crystallised from methanol, gave needles, m.p. 171° (lit.[6] m.p. 169°), $[\alpha]_D$ + 69·7° (c, 0·85%).

Acetylation with acetic anhydride and heating of the product in 70% ethanol for 2 hrs. (to destroy the mixed anhydride) gave needles from methanol, m.p. and mixed m.p. 287-289° (lit.[6, 7] m.p. 293-294°, 289-290°), $[\alpha]_D$+70·1° (c, 0·85%) [Found: C, 77·15; H, 10·1. Calc. for $C_{32}H_{50}O_4$: C, 77·06; H, 10·1%]. The infrared spectrum coincided with that of authentic material.

Ursolic acid methyl ester acetate, prepared with diazomethane and crystallised from methanol, gave needles, m.p. 247-249° (lit.[6] 245°), $[\alpha]_D$ + 65·4° (c, 0·8%) [Found: C, 77·4; H, 10·3. Calc. for $C_{33}H_{52}O_4$: C, 77·3; H, 10·2%].

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NOTES

THE ISOLATION OF RADIOSILVER BY ISOTOPIC EXCHANGE

by

M. PEISACH and S. J. VAN DER WALT

Meinke and Sunderman[1] showed that sources of silver-111 could be prepared by isotopic exchange between dissolved and solid silver salts, and that about 98% recovery could be obtained with 5 mg silver carrier in the form of silver iodide on an inert grid. Since for nuclear spectroscopy it is essential that the amount of carrier should be as low as possible, this investigation was undertaken to determine how far the weight of silver iodide could be reduced without seriously affecting the recovery of radiosilver.

EXPERIMENTAL

Platinum grids were coated with varying weights of silver iodide by electroplating silver at 3 volts from a solution of 3M sodium cyanide, 0·5M sodium hydroxide and 0·01M silver nitrate, and converting it to iodide by electrolysis at 1·5 volts in a solution of 0·05M hydrogen iodide and 0·05M sodium bisulphite. The grids were washed and stored in 1:1 nitric acid.

For the exchange reaction the coated grids were rotated in a solution of radiosilver and the course of the reaction was followed by periodically measuring the activity of the solution. A plot of the percentage activity removed from solution against the duration of exchange is shown in Fig. 1 for grids with 1·45, 0·89, 0·23 and 0·14 mg silver iodide respectively. For small weights of silver iodide recovery is poor, and begins to fall sharply within a reasonably short time due to the photolytic decomposition of silver iodide. For recoveries of about 70% about 1 mg silver iodide is required.

To recover the isolated radiosilver, the silver iodide was dissolved in a solution of 3M sodium cyanide and 0·05M sodium hydroxide, and the silver was electroplated on to a platinum needle at 3 volts. The potential was then raised to 3·5 volts while the electrode was removed from solution and washed with a 1% solution of sodium nitrate. Fig. 2 shows the dependence of the rate of deposition of silver on the initial concentration of silver. For low concentrations of silver initial electrolysis removes the silver ions from solution in the immediate vicinity of the electrode and subsequent deposition will depend on the diffusion of ions towards the electrode. Accordingly, with decreasing concentration of silver there will be a large increase in the time required to recover the bulk of the silver. It can be shown from calculations of deposition rates that this method is impractical for the recovery of short-lived silver isotopes such as silver-112 and silver-113 and can be applied to longer-lived isotopes only when the weight of silver iodide carrier exceeds about 1 mg.

From the study of the exchange reaction as well as the subsequent recovery of exchanged silver by electrodeposition it is concluded that about 1 mg silver iodide is required. Since this amount of carrier produces a relatively thick source, the method of isotopic exchange cannot be used to prepare sources of radiosilver for nuclear spectroscopy.

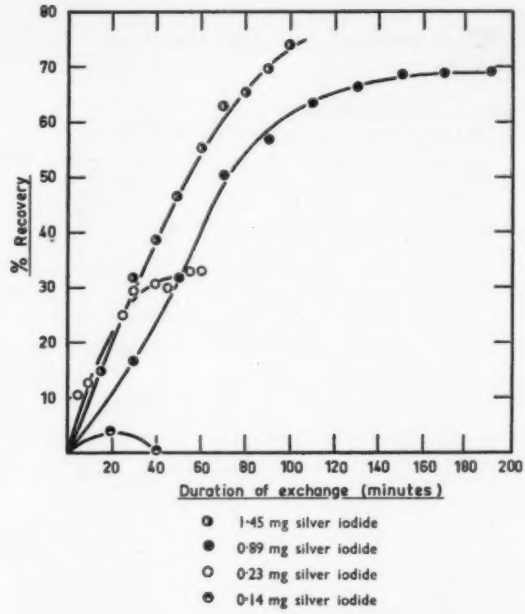

FIG. 1—The effect of the weight of silver iodide on the exchange reaction

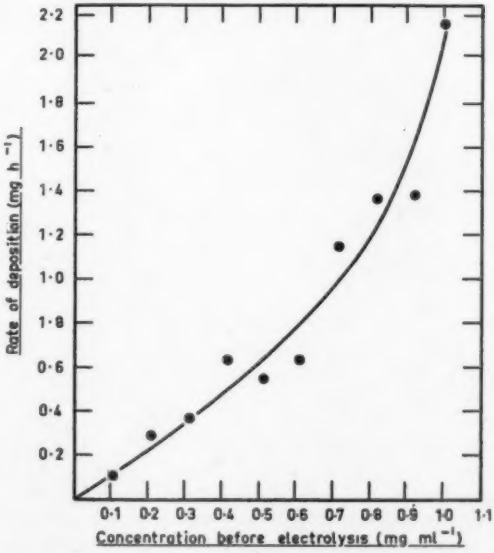

FIG. 2—The effect of concentration on the electrolysis of silver

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